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⑪ Publication number : **0 602 865 A1**

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EUROPEAN PATENT APPLICATION

⑳ Application number : **93309782.6**

⑤① Int. Cl.⁵ : **B01D 53/36, B01J 23/56,
B01J 37/03**

㉔ Date of filing : **06.12.93**

③① Priority : **18.12.92 GB 9226434**

④③ Date of publication of application :
22.06.94 Bulletin 94/25

⑧④ Designated Contracting States :
**AT BE CH DE DK ES FR GB GR IE IT LI NL PT
SE**

⑦① Applicant : **JOHNSON MATTHEY PUBLIC
LIMITED COMPANY**
78 Hatton Garden
London, WC1N 8JP (GB)

⑦② Inventor : **Rajaram, Raj Rao**
78 Norfolk Avenue
Slough, Berks, SL1 3AD (GB)
Inventor : **Hayes, John William**
5 Elm Court
Sonning Common, Reading RG4 9ND (GB)
Inventor : **Ansell, Graham Paul**
1 Thornbury Green
Twyford, Berks, RG10 9RH (GB)
Inventor : **Hatcher, Helen Anne**
79 Kings Road
Caversham, Reading RG4 8DS (GB)

⑦④ Representative : **Brewer, Leonard Stuart et al**
Patents Department
Johnson Matthey Technology Centre
Blounts Court
Sonning Common
Reading Berkshire RG4 9NH (GB)

⑤④ **Catalyst.**

⑤⑦ A reaction comprising the oxidation of carbon monoxide to carbon dioxide, eg in vehicle exhausts, employs a catalyst composed of metal oxide, eg ceria, particles among which are uniformly incorporated noble metal particles, the particles having such a high interaction that, without hydrogen reduction pre-treatment, the catalyst exhibits the formation of anionic vacancies on the metal oxide surface at a temperature lower than does the corresponding catalyst prepared by impregnation. The catalyst employed is preferably prepared by co-precipitation.

EP 0 602 865 A1

This invention relates to a method of conducting a chemical reaction comprising the oxidation of carbon monoxide to carbon dioxide employing a catalyst, to an engine whose exhaust apparatus contains the catalyst in order to combat air pollution, to a certain such catalyst containing ceria and its preparation and use, and to the preparation of ceria.

5 Transition metal catalysts, especially those involving Group VIII metals, are usually prepared by dispersing the active component on high surface area carriers, such as refractory inorganic oxides, to achieve maximum specific metal surface areas and high thermal stability. The support material must usually have a high surface area, and various parameters are considered in selecting a support for metal catalysts. Metal oxides are the most commonly used carrier, and their dominance is a consequence of their generally high thermal and chemical stability, coupled with the knowledge of preparation of the materials with high surface areas. Support materials can be classified into either inert supports, like SiO_2 , supplying high surface area for dispersing the active component, or catalytically active supports, like $\text{SiO}_2\text{-Al}_2\text{O}_3$ or zeolite, for bifunctional catalysts. The nature of the carrier oxide can affect the size and morphology of the metal particles, either during deposition or activation, an effect generally referred to as non-specific metal-metal oxide interaction. In certain other cases, the support can influence the active component by a strong interaction, an example being partially reduced TiO_2 . Support for the view that the metal oxide support can significantly influence the catalytic properties of the metal in a more specific manner was provided by Tauster and co-workers (US patent specification 4149998) who described the unusual effects observed in certain metal-metal oxide systems and introduced the acronym SMSI (strong metal support interaction). The SMSI phenomenon, caused by the high temperature reduction of Group VIII metals dispersed on certain metal oxides, is characterised by a suppression in the metal's ability to chemisorb CO or H_2 , increased catalytic activity in CO/ H_2 reactions, and decreased activity for structure sensitive reactions such as alkane hydrogenolysis, and is reversible in the sense that mild oxidation will restore the catalyst to its original state. The dispersion of the metal particles, thus the metal-metal oxide interfacial area, and the temperature of H_2 reduction will both influence the extent of the SMSI effect. The various hypotheses invoked to explain the SMSI phenomenon include explanations involving a geometric effect caused by migration of oxidic moieties from the support to the surface of the metal particles, an electronic effect caused by charge transfer from cations on the oxide surface to the metal, or the creation of new active sites at the metal-metal oxide interface.

The concept that a H_2 reduction pre-treatment could influence catalytic activities of metals supported on metal oxides to enhance the low temperature CO oxidation activities of certain metal-metal oxides catalysts has been described in various patent specifications, for instance European patent specification 0337446. These do not specify whether the induced changes are due to a SMSI-type effect or the simple reduction of the metal component. The advent of automobile exhaust catalysts has led to further intensive investigations of the interaction of noble metals with metal oxides, notably CeO_2 . Yu Yao (J of Catalysis, 87, 152-162 (1984)) has shown that treatment of Pd, Pt or Rh catalysts supported on $\text{CeO}_2\text{-Al}_2\text{O}_3$ under reducing conditions results in a dramatic, but transient, enhancement of catalytic activity for the oxidation of CO and hydrocarbons. Other research groups have studied specifically the Pt- CeO_2 interaction after reduction pre-treatment and have shown enhancement in conversion activity for CO oxidation and NO_x reduction. The degree of the Pt- CeO_2 interaction was dependent on both the Pt and CeO_2 crystallite sizes. The catalysts were designed to achieve highly dispersed Pt on high surface area CeO_2 (for high Pt- CeO_2 interfacial area) by impregnation techniques, prior to the reduction pre-treatment.

The strong metal-metal oxide interaction described in this prior literature has been observed on catalysts prepared by conventional impregnation techniques. Such procedures do not lead to a material with intrinsically unique or unusual catalytic properties. The treatment of these systems in a reducing atmosphere at high temperature induces the reported unique properties and activities of these catalysts. In addition, many of these systems are reversible in that a subsequent treatment in an oxidising atmosphere at a certain temperature, normally greater than 200°C , negates these unique catalytic properties and therefore reverses any changes in the structure or electronic character which account for the unique catalytic properties and can severely impair the usefulness of such catalyst systems.

50 The present invention relates to metal-metal oxide catalysts which have unique and unusual catalytic properties which are intrinsic, not requiring a separate reduction pre-treatment to manifest them, and which are stable, not being reversible in nature.

Accordingly, the invention provides a method of conducting a chemical reaction comprising the oxidation of carbon monoxide to carbon dioxide employing a catalyst composed of metal oxide particles among which are uniformly incorporated noble metal particles, the catalyst having such a high interaction between the noble metal particles and the metal oxide particles that, without hydrogen reduction pre-treatment, it exhibits the formation of anionic vacancies on the metal oxide surface at a temperature lower than does the corresponding catalyst, without hydrogen reduction pre-treatment, containing the same amount of the metal oxide particles

and noble metal particles and prepared by impregnating the metal oxide particles with noble metal precursor and calcining to convert the precursor to the noble metal particles.

The invention provides also an engine whose exhaust apparatus contains the catalyst in order to combat air pollution.

5 The invention also provides as a novel composition of matter the catalyst wherein the metal oxide comprises CeO_2 and the noble metal is one or more of Pt, Pd, Rh and Au.

The invention provides also a process for preparing a catalyst composed of metal oxide particles comprising CeO_2 among which are uniformly incorporated noble metal particles, the noble metal being one or more of Pt, Pd, Rh and Au, which process comprises co-precipitating the noble metal particles and the metal oxide
10 particles comprising CeO_2 .

The invention also provides a method of conducting a chemical reaction employing the catalyst wherein the metal oxide comprises CeO_2 and the noble metal is one or more of Pt, Pd, Rh and Au.

The invention provides also a process for preparing ceria, which process comprises adding a solution of ceria precursor to a solution of a base to precipitate cerium hydroxide and heating the cerium hydroxide to
15 convert it to ceria.

By noble metal is meant in this specification one or more of Ru, Rh, Pd, Os, Ir, Pt and Au. Preferably, the noble metal is one or more of Pt, Pd, Rh and Au, especially one or more of Pt, Pd and Rh. The catalyst usually contains 0.1 to 30% by weight of the noble metal particles based on the total weight of the noble metal particles and the metal oxide particles. In one embodiment, the catalyst contains 0.1-10% by weight Pt and 0.1-20%
20 by weight palladium on this basis, for instance when the metal oxide is CeO_2 .

The metal oxide preferably comprises (ie consists of or includes) one or more of CeO_2 , ZrO_2 , TiO_2 and SnO_2 , especially one or more of CeO_2 , ZrO_2 and SnO_2 , particularly CeO_2 . The metal oxide preferably contains 80-100% by weight of such oxides. To increase the thermal stability of the catalyst, particularly when CeO_2 is employed as metal oxide, the metal oxide can include a minor amount of a secondary metal oxide to decrease
25 the extent of sintering the main metal oxide during high temperature exposure. The amount of secondary metal oxide, when it is employed, is usually between 1 and 20% by weight of the metal oxide. The secondary metal oxide can be, for instance, one or more of ZrO_2 , Al_2O_3 , La_2O_3 and BaO , particularly ZrO_2 and/or Al_2O_3 .

The present catalyst has the noble metal particles uniformly incorporated among the metal oxide particles. The interaction between the two sets of particles is accordingly even and contrasts, for instance, with metal
30 oxide particles whose surface has been impregnated with a noble metal precursor and which have been calcined to convert the precursor to noble metal particles. In addition, the interaction between the two sets of particles in the present catalyst is of unique type, as discussed above. The interaction between the noble metal particles and the metal oxide particles is so high that, without hydrogen reduction pre-treatment, the catalyst exhibits the formation of anionic vacancies on the metal oxide surface at a temperature lower, usually by at
35 least 40°C, preferably by at least 80°C, especially by at least 200°C, than does the corresponding catalyst, without hydrogen reduction pre-treatment, prepared by impregnation. The corresponding catalyst prepared by impregnation contains the same amount of the metal oxide particles and the same amount of the noble metal particles, but has been prepared by impregnating the metal oxide particles with noble metal precursor and calcining to convert the precursor to the noble metal particles. This is the well known, conventional, meth-
40 od of preparation. As discussed above, hydrogen reduction pre-treatment has been required in the past in order to activate catalysts composed of metals and metal oxides to a strong metal-metal oxide interaction. The formation of anionic vacancies on the metal oxide surface enables the present catalyst to catalyse reactions such as those comprising the oxidation of carbon monoxide to carbon dioxide. The temperature at which the formation of anionic vacancies is exhibited is conveniently found by temperature programmed reduction. This
45 analytical technique shows the temperature at which reduction of surface anion, and hence the formation of anionic vacancies, occurs. The temperature at which the corresponding catalyst prepared by impregnation exhibits the formation of anionic vacancies can be found by the same analytical technique, but is generally given in the literature, for instance (1) Yao H C and Yu Yao Y F, J of Catalysis, 86, 254 (1984) and (2) Diwell A F, Rajaram R R, Shaw H A and Truex T J, "Studies in Surface Science and Catalysis", vol 71 (Capoc II),
50 edited by Crucq A and published by Elsevier (1991), page 139.

The metal-metal oxide interaction in the present catalyst involves a high metal-metal oxide contact area. Accordingly, the size of their particles should be small. The noble metal particle diameter is preferably less than 10Å. The metal oxide particle diameter is preferably up to 250Å, for instance 10-250Å.

In a particular embodiment, the metal oxide phase partially or completely encapsulates the metal particles, resulting in significant suppression of the carbon monoxide chemisorption ability of the metal particles.
55 For instance, when the noble metal is Pt and the metal oxide CeO_2 , the carbon monoxide chemisorption value of CO:noble metal is preferably less than 0.2.

The strong metal-metal oxide interaction in the present catalyst permits the reduction of surface anions

on the oxide surface at unusually low temperature. The catalyst is preferably such that tested on the simulated car exhaust gas mixture defined in Table 4 hereafter under conditions rich of stoichiometric at $\lambda=0.98$ and at a mass hourly space velocity of 60 litres of gas mixture per hour per g of catalyst, it converts one or more, preferably two or three, and especially all three, of:

- 5 (a) 50% of the CO at a temperature lower than 250°C, preferably lower than 150°C;
- (b) 50% of the NO at a temperature lower than 300°C, preferably lower than 250°C; and
- (c) 50% of the C_3H_8 at a temperature lower than 350°C, preferably lower than 300°C.

The present catalyst, with its high metal-metal oxide interaction, is preferably that preparable by co-precipitation of the noble metal particles and the metal oxide particles. Co-precipitation is a very effective method of incorporating the noble metal particles uniformly among the metal oxide particles to achieve their high interaction. The co-precipitation can be carried out in a manner known generally per se. Although co-precipitation of noble metal particles and metal oxide particles is known in certain instances, for example from (A) European patent specification 457480 and (B) Koeppel et al, J Chem Soc, Faraday Trans, 87, 17, page 2821 (1991), it was not realised before that catalysts prepared in this way are so advantageous in chemical reactions comprising the oxidation of carbon monoxide to carbon dioxide. The present catalyst wherein the metal oxide comprises CeO_2 and the noble metal is one or more of Pt, Pd, Rh and Au, is a novel composition of matter, and the invention provides it as such. Co-precipitating the noble metal particles and the metal oxide particles comprising CeO_2 automatically gives the high interaction between the two sets of particles which is characteristic of the present catalyst and which is evident from its exhibiting, without hydrogen reduction pre-treatment, the formation of anionic vacancies on the metal oxide surface at a temperature lower than does the corresponding catalyst, without hydrogen reduction pre-treatment, prepared by impregnation.

It will be understood that the present co-precipitation may produce a precipitate which does not have the metal oxide present as such but in a form, such as an hydroxide, which is then converted to the metal oxide. The conversion can be accomplished for instance by heating, for example at 50-500°C.

The present co-precipitation is carried out preferably at 50-120°C, especially from boiling aqueous solution. The co-precipitation is preferably carried out so that it occurs in a controlled rather than a sudden manner. In certain cases, while forming the high metal-to-metal oxide interfacial area, partial or complete encapsulation of the metal particles by the oxide phase occurs, resulting in significant suppression of the carbon monoxide chemisorption ability of the well dispersed metal particles. The co-precipitation method generates the metal-metal oxide interaction without requirement for reduction in hydrogen to manifest it, and also stabilises the interaction, as it is maintained even after air calcination at high temperature (for instance at a temperature between 500 and 900°C).

In one aspect of preparation, in the co-precipitation the noble metals particles, particularly of one or more of Pt, Pd, Rh and Au, are co-precipitated from colloid of the metal. The colloid can be pre-formed. For instance, a Pt colloid sol can be made by reduction of chloroplatinic acid with ethanol in the presence of a stabilising agent. In a particular technique, the co-precipitation is effected by admixing noble metal colloid, a solution of metal oxide precursor, and a base. The noble metal colloid can be formed in situ by a reducing agent.

In another aspect of preparation, in the co-precipitation the noble metal particles, particularly of one or more of Pt, Pd and Au, are co-precipitated by reduction of hydrolysed noble metal salt. In this aspect of preparation, the catalyst usually contains 0.5-20, preferably 0.5-5, % by weight of the noble metal particles based on the total weight of the noble metal particles and the metal oxide particles. The noble metal salt which is hydrolysed can be any convenient soluble salt; in the case of platinum, for instance, chloroplatinic acid, tetraammine platinum hydroxide or tetraammine platinous chloride can be employed. The hydrolysis can be brought about by a base. The reduction can be brought about by a reducing agent. Peculiar to the case of metal oxide being CeO_2 , metal oxide precursor is advantageously used to reduce the hydrolysed metal salt. This is very surprising; such a possibility has never been alluded to in the prior art. In this case, the cerium oxide precursor must be Ce^{3+} salt in solution; as illustrated hereafter, corresponding use of a cerium oxide precursor in the form of Ce^{4+} salt in solution does not produce the present catalyst with its unique structure and advantageous properties. The Ce^{3+} salt can be any soluble Ce^{3+} salt.

In the present preparation, any soluble base can generally be used as precipitant, such as NaOH, KOH, NH_4OH or an organic base. The preferred base is NaOH. Precipitation of the metal oxide can be brought about by reaction of a solution of a base and a solution of metal oxide precursor. The metal oxide precursor can be any soluble salt which can be converted to metal oxide in this way, except for the special case involving the cerium oxide precursor, when used as reducing agent, being in the Ce^{3+} form as discussed above (but the cerium oxide precursor can be a salt in which the cerium is in any oxidation state in the aspect involving a noble metal colloid). When the metal oxide in the catalyst includes a secondary metal oxide as discussed above, the secondary metal oxide can be incorporated during the co-precipitation by similarly precipitating it from a solution of a salt. Any reducing agent in the present preparation can be for instance formaldehyde or

sodium formate.

In the present preparation involving a solution of a base, a solution of metal oxide precursor is preferably added to the solution of the base, so that the precipitation is reached from the basic side, rather than the solution of the base being added to the solution of the metal oxide precursor, so that the precipitation is reached from the acidic side. It has been found that this preferred order of addition tends to result in a catalyst of higher surface area, particularly when the metal oxide is CeO_2 .

It has been found that this order of addition is thus advantageous in the case of CeO_2 whether or not the present noble metal moiety is employed; CeO_2 of surprisingly higher surface area is produced. Accordingly, the invention provides a process for preparing ceria, which process comprises adding a solution of ceria precursor to a solution of a base to precipitate cerium hydroxide and heating the cerium hydroxide to convert it to ceria. The process can be conducted in the same way as the co-precipitation described herein except that the noble metal moiety need not be present; a different or no catalytically active component moiety can be employed instead of the noble metal moiety. The base is preferably NaOH . The cerium hydroxide precipitated can be Ce^{3+} hydroxide or Ce^{4+} hydroxide. The hydroxide is usually heated in air. It is usually heated at a temperature of $50\text{--}500^\circ\text{C}$. The ceria usually has a Brunauer Emmett Teller surface area of at least $100\text{m}^2\text{g}^{-1}$. The ceria is advantageously used as a component of a catalyst. The component can be catalytically active or a carrier.

The present catalyst has a high metal-metal oxide interaction, so as to promote the reduction of surface anions on the oxide surface at unusually low temperature. Temperature programmed reduction, a technique routinely used to characterise supported metal catalysts, can be used to identify the desirable interaction. It is known that the presence of a metal can sometimes catalyse the reduction of an oxide by providing spillover atomic hydrogen, which first creates OH_s^- groups with the surface lattice anions. The dehydration of these OH_s^- groups will then lead to the formation of anionic vacancies. Yao and Yu Yao, in their reference specified above, have suggested, for instance, that there are two kinds of lattice oxygen in CeO_2 , which can be removed by H_2 at 500°C and 800°C respectively. The addition by conventional impregnation technique of a noble metal such as Pt, Rh or Pd to CeO_2 will catalyse the reduction of the first type of oxygen, associated with conversion of surface oxide anion to oxygen vacancy, and not the second type of oxygen, the bulk oxygen anion, suggesting that the metal interacts mainly with the surface of the oxide. The high metal-metal oxide interaction in the present invention enables the formation of such vacancies at lower temperature than that observed for corresponding impregnated catalysts. The mechanism by which the metal promotes the production of anionic vacancies on the oxide surface in the present invention may not necessarily be due to the spillover of atomic hydrogen from the metal to the oxide, as gold, a metal known for its inability to dissociate hydrogen, promotes the effect in the present invention.

The present catalyst wherein the metal oxide comprises CeO_2 and the noble metal is one or more of Pt, Pd, Rh and Au is remarkably effective in catalysing chemical reactions. It can be employed without hydrogen reduction pre-treatment. It can be employed after a calcination pre-treatment in air at between 300 and 900°C , usually between 500 and 900°C . The catalyst is particularly useful when employed for conducting reactions at lower temperatures than previously were employed. It is especially useful where the reaction is a redox reaction. The present catalyst is remarkably effective in catalysing a chemical reaction comprising the oxidation of carbon monoxide to carbon dioxide. Again, the catalyst, whether or not the metal oxide comprises CeO_2 and the noble metal is one or more of Pt, Pd, Rh and Au, can be employed without hydrogen reduction pre-treatment. Again, the catalyst can be employed after a calcination pre-treatment in air at between 300 and 900°C , usually between 500 and 900°C . Again, it is particularly useful when employed for conducting reactions at lower temperatures than previously were employed. The catalyst is especially useful for the oxidation of carbon monoxide and hydrocarbon to carbon dioxide and water and the reduction of nitrogen oxides to nitrogen. The catalyst can be used for conducting this particular reaction in the exhaust apparatus of an engine, especially an internal combustion engine in a vehicle, in order to combat air pollution. The catalyst is of particular interest, because of its low temperature activity, for the treatment of vehicle exhaust emissions at low temperature during warm-up.

The present catalyst can be employed as the sole catalyst or together with another catalyst, usually comprising one or more of Pt, Pd and Rh, for instance Rh optionally with Pt and/or Pd. The present catalyst can be formulated in the usual way to catalyse chemical reactions. When it is employed as sole catalyst, it generally does not need a separate high surface area carrier such as is discussed above in relation to transition metal catalysts. When it is employed together with another catalyst, a high surface area carrier is often useful to carry both catalysts. For instance, the present catalyst can be dispersed on the carrier and, either before or usually afterwards, the other catalyst can be dispersed on the carrier, for instance in the usual way by impregnating with a precursor and calcining to convert the precursor to the other catalyst. The present catalyst itself preferably has a Brunauer Emmett Teller surface area of at least 50 , especially at least 100 , m^2g^{-1} . The

catalyst can be employed in the form of pellets. It can be employed on a support, preferably a monolith, for instance a honeycomb monolith. The monolith can be metal, in which case it can readily be heated, for instance by passing an electrical current through the metal. Alternatively, the monolith can be ceramic. A separate heater of gas can be utilised up-stream of the catalyst to heat gas to facilitate its reaction on the catalyst.

The invention is illustrated by the accompanying drawings, whose 26 Figures are described in the Examples hereafter.

The invention is illustrated by the following Examples.

EXAMPLE 1

Preparation of Ceria

Ceria was prepared using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (126g) and solid NaOH (36g). The NaOH was dissolved in 6 litres of de-ionised water and brought to the boil. The $\text{Ce}(\text{NO}_3)_3$ was dissolved in water and made up to 500cm³. The resulting solution was added dropwise to the boiling NaOH solution to produce a greyish white precipitate. The addition of the Ce^{3+} solution usually lasted over an hour and the final pH was normally about 10. The precipitate was boiled for a further hour, filtered, and then washed free of NO_3^- and Na^+ . The washed precipitate was dried at 110°C and then calcined in air at 500°C. Its BET surface was 136m²g⁻¹.

EXAMPLE 2

Pt-CeO₂ Catalyst made by co-precipitation using Ce³⁺ precursor

50g of Pt-CeO₂ catalyst with a nominal loading of 0.9wt% Pt was prepared using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (126g), chloroplatinic acid (1.148g - Pt assay 39.20wt%) and solid NaOH (36g). The NaOH was dissolved in 6 litres of de-ionised water and brought to the boil. The CPA and $\text{Ce}(\text{NO}_3)_3$ were dissolved in water and made up to 500cm³ as a single solution. The latter was added dropwise to the boiling NaOH solution to produce a black precipitate. The addition of the CPA/ Ce^{3+} solution usually lasted over an hour and the final pH was normally about 10. The precipitate was boiled for a further hour, filtered, and then washed free of NO_3^- , Cl^- , and Na^+ . The washed precipitate was dried at 110°C and then calcined in air at 500°C.

To illustrate the strong Pt-CeO₂ interaction achieved by this preparative route, as opposed to a standard impregnation route, a Pt-CeO₂ catalyst containing 0.9wt% Pt was made by incipient wetness of CeO₂ (prepared as described in Example 1) with chloroplatinic acid. After drying at 110°C, the sample was calcined at 500°C. Similarly, to define the unique role of Ce³⁺ during the co-precipitation another sample of Pt-CeO₂ was made by co-precipitation using Ce⁴⁺ precursor (cerium ammonium nitrate). This sample is 50g of Pt-CeO₂ catalyst with a nominal loading of 0.9wt% Pt and was prepared using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (159.3g), chloroplatinic acid (1.148g - Pt assay 39.20wt%) and solid NaOH (48g). The NaOH was dissolved in 6 litres of deionised water and brought to the boil. The CPA and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ were dissolved in water and made up to 500cm³ as a single solution. The latter was added dropwise to the boiling NaOH solution to produce a beige colour precipitate. The slurry was boiled for a further hour, filtered, and then washed free of NO_3^- , Cl^- , and Na^+ . The washed precipitate was dried at 110°C and then calcined in air at 500°C. Analysis of these samples has confirmed a Pt loading of 0.9wt%.

The BET surface areas and CO chemisorption values (the ratio of CO chemisorbed at room temperature to Pt) of the samples calcined at 500°C are shown in Table 1.

The strong Pt-CeO₂ interaction is typified by the low CO chemisorption value of the catalyst prepared by the co-precipitation route using Ce³⁺ precursor.

Table 1

Catalyst Calcined 500°C	Preparative route	BET SA m ² g ⁻¹	CO Chem CO:Pt
0.9%Pt-CeO ₂	Ce ³⁺ + CPA → NaOH	130	0.08
0.9%Pt-CeO ₂	Ce ⁴⁺ + CPA → NaOH	125	0.54
0.9%Pt/CeO ₂	Impregnation	136	0.71

Transmission electron microscopy can be used to provide information on the location and the size of metal particles dispersed on an oxide support. HRSTEM (high resolution scanning transmission electron microsc-

py) micrographs of the Pt-CeO₂ catalysts showed very small ceria crystallites (1-25nm) in all samples. No images of Pt could be recorded, even at a magnification of 25 x 10⁶, indicating particles probably less than 1nm in size (NB, Pt particles greater than 10nm have been observed on the same instrument, despite the poor contrast between the support and the particles). EDAX (energy dispersive x-ray analysis) has shown Pt dispersed in dense areas of CeO₂; the signal was very weak for the co-precipitated catalyst using Ce³⁺, indicating possibly platinum dispersed throughout the sample, whereas a much more intense signal was recorded for the other catalysts, indicating that in the latter cases the Pt was most probably dispersed on the surface.

X-ray photoelectron emission spectroscopy (XPS) can detect the electronic state of the catalyst and possibly the location of the metal particles, as the depth of analysis is only a few atomic layers from the surface. The results are summarised in Table 2. Ce was present as Ce⁴⁺ in all three samples. Catalysts prepared by impregnation or using Ce⁴⁺ precursor show well defined Pt peaks in the XPS spectra, with Pt in a +2 oxidation state, Figure 1a. However, catalyst prepared by co-precipitation using Ce³⁺ precursor produced poorly resolved Pt peaks, indicating that the Pt was not totally located on the oxide surface, Figure 1b.

Table 2

Sample	Preparative Route	Ce Oxidation state	Pt Oxidation state	Pt/Ce Atomic ratio
Pt-CeO ₂	Ce ³⁺ + CPA → NaOH	Ce ⁴⁺	Undefined	0.002
Pt-CeO ₂	Ce ⁴⁺ + CPA → NaOH	Ce ⁴⁺	Pt ²⁺	0.011
Pt/CeO ₂	Impregnation	Ce ⁴⁺	Pt ²⁺	0.016

Extended x-ray absorption fine structure (EXAFS) spectra (Pt L edge) for the different Pt-CeO₂ samples, calcined at 500°C, were recorded to provide information about the chemical environment of Pt. The Pt distances used for analysis were those of face-centred cubic Pt and PtO₂. The Pt L edge spectra obtained were fitted to those of the reference materials and a summary of the properties derived is given in Table 3.

Table 3

Sample	Preparative route	EXAFS data	
		%Pt	%PtO ₂
Pt-CeO ₂	Ce ³⁺ + CPA → NaOH	70	30
Pt-CeO ₂	Ce ⁴⁺ + CPA → NaOH		100
Pt/CeO ₂	Impregnation		100

The catalysts prepared by impregnation or using Ce⁴⁺ precursor contain Pt in a high oxidation state. However, the sample prepared by co-precipitation using Ce³⁺ precursor has a significant portion of Pt in a metallic state. Metallic Pt particles of a similar type were present, if the impregnated catalyst was reduced in H₂ at 600°C.

The apparent discrepancy between the Pt oxidation state of IV, indicated by EXAFS in Table 2, and II indicated by XPS in Table 3, in some samples is thought to be due to the material being observed at or towards the surface of the catalyst by XPS and in the bulk of the catalyst by EXAFS. The important point is that both techniques are consistent in indicating well-dispersed platinum in the catalyst prepared by co-precipitation using Ce³⁺ precursor, with EXAFS further indicating that a large proportion of this is in the form of Pt(0).

The Pt-CeO₂ catalyst, prepared by co-precipitation using Ce³⁺ precursor, possesses a geometric and electronic structure which is significantly different to the other catalysts. These unique features result in a strong metalmetal oxide interaction which can be characterised by the temperature required to form anionic vacancies on the oxide surface, during temperature programmed reduction (tpr). The tpr spectrum of CeO₂ is shown in Figure 2. The presence of two peaks is attributed to two types of oxygen anion in CeO₂; the low temperature peak is associated with the reduction of surface anion, whilst the high temperature peak is associated with the bulk reduction of CeO₂ to Ce₂O₃. The addition of Pt to CeO₂ by impregnation lowers the position of the

first peak, indicating the Pt-CeO₂ interaction is mostly a surface effect, Figure 3, which agrees with the data for this impregnated catalyst in the literature, for instance the Yao and Yu Yao reference specified above. (NB, a small fraction of the hydrogen consumed in the first peak is due to reduction of the platinum oxide). A similar effect is noted from the tpr profile of the co-precipitated catalyst using Ce⁴⁺ precursor, again shown in Figure 3 as the trace is substantially identical to that of the impregnated catalyst. The mechanism by which Pt promotes the reduction of surface anion of CeO₂ is by the spillover effect described previously. The tpr spectrum of the catalyst prepared using Ce³⁺ precursor is significantly different, Figure 4. H₂ consumption is noted to start at much lower temperature, providing a peak at significantly lower temperature to that noted for the other Pt-CeO₂ catalysts. The process is associated mostly with the reduction of surface anion to anionic vacancies in the CeO₂ (EXAFS has indicated that Pt is present mostly in a metallic state in the catalyst and therefore cannot contribute significantly to the reduction profile). Furthermore, the tpr spectrum of the catalyst shows an intermediate peak which corresponds to that for the reduction of surface anion on non-metallised CeO₂; the complete peak was shifted to lower temperature for the impregnated catalyst. The strong metal-metal oxide interaction caused by preparing Pt-CeO₂ catalyst by co-precipitation, using Ce³⁺ precursor, induces anionic vacancy formation in the oxide at low temperature. The effect, however, may not be due to a simple spillover mechanism as observed for the impregnated catalyst, since the reduction of a fraction of the surface anion was not catalysed by the metal and a significant fraction of the metal particles was not localised on the surface. The co-precipitated catalyst prepared via Ce³⁺ precursor is very different in its architecture to the catalysts prepared by impregnation or co-precipitation with Ce⁴⁺ precursor. The unique activity of these systems is illustrated by their ability to convert CO, NO and alkene at low temperature. This is demonstrated in Figures 5-7, which also include the activities of the impregnated catalyst and co-precipitated Ce⁴⁺ catalyst. The activity was measured in a simulated gas mixture rich of stoichiometric (Table 4) at lambda=0.98.

Table 4

Composition of simulated exhaust gas at $\lambda=0.98$	
Composition	Concentration / mol%
H ₂	0.43
O ₂	0.72
CO	1.30
CH ₄	0.067
C ₃ H ₈	0.0223
C ₃ H ₆	0.0223
CO ₂	15.0
H ₂ O	9.2
NO	0.15
SO ₂	0.002
N ₂	Balance

EXAMPLE 3**Au-CeO₂ Catalyst made by co-precipitation using Ce³⁺ precursor**

50g of Au-CeO₂ catalyst, with a nominal loading of 0.9wt% Au, was prepared using HAuCl₄ (0.912g - assay 49.36wt% Au), Ce(NO₃)₃·6H₂O (126g) and solid NaOH (35.91g). The preparative method was similar to that used in Example 2 for the Pt-CeO₂ catalyst. Initially, a very fine black precipitate was produced, but on boiling, a dark purple catalyst was obtained. A 0.9wt% Au-CeO₂ catalyst was also made by impregnation of HAuCl₄ on CeO₂.

The tpr spectrum of the catalysts after calcination at 500°C in air is shown in Figures 8 and 9 for the impregnated and co-precipitated catalyst respectively. The impregnated catalyst has a tpr profile similar to that of unmetallised CeO₂ (Figure 2) indicating the inability of Au to provide spillover atomic hydrogen. The strong metal-metal oxide interaction achieved by co-precipitation, using Ce³⁺ precursor, is again characterised by the uptake of hydrogen at low temperature, due to the formation of anionic vacancies.

The co-precipitated Au-CeO₂ catalyst was similarly capable of converting CO, NO and alkene at lower temperature than the impregnated catalyst, under simulated exhaust condition specified in Table 4 above. The activity of the impregnated catalyst was similar to that of unmetallised CeO₂, which was insignificant at temperature below 300°C. The CO and NO conversions at 200°C at lambda=0.98 are given in Table 5:

Table 5

Catalyst	Preparative Route	CO Oxidation	NO Reduction
Au-CeO ₂	Co-precipitated	55%	45%
Au-CeO ₂	Impregnated	0%	0%

EXAMPLE 4

Pd-CeO₂ Catalyst made by co-precipitation using Ce³⁺ precursor

50g of Pd-CeO₂ catalyst with a nominal loading of 0.9wt% Pd was prepared using Ce(NO₃)₃ (126g), Pd(NO₃)₃ (5.57g - assay 8.08% Pd) and solid NaOH (36g). The preparative route is as described in Example 2.

The ability of the metal to promote vacancy formation on the oxide surface at low temperature is illustrated by the tpr spectrum of the sample calcined at 500°C, Figure 10. The activity of the catalyst measured in a simulated exhaust condition, rich of stoichiometric at lambda=0.98, shown in Figure 11, again indicates the capability of these catalysts to convert CO, NO and alkene at low temperature.

EXAMPLE 5

Bi-metallic Pd-Pt-CeO₂ Catalyst made by co-precipitation using Ce³⁺

A Pd-Pt-CeO₂ catalyst of high thermal stability and intrinsic activity for CO, NO, and alkene was made by co-precipitating Pt, Pd with CeO₂. The Pt loading was 0.5wt% and the Pd loading was 4wt%.

Palladium nitrate (26.04g - assay 7.68wt% Pd), chloroplatinic acid (0.638g - assay 39.2wt% Pt) and cerous nitrate (126g) were dissolved in 500cm³ of de-ionised water. 40g NaOH was dissolved in 6 litres of water and brought to the boil. The Pd-Pt-Ce³⁺ solution was added dropwise to the NaOH solution to achieve a black precipitate which was then filtered, washed, dried and calcined in air at 500°C. Additionally Ni could be added to the catalyst either during co-precipitation or post-impregnation, to act as an H₂S getter.

The bi-metallic catalyst has features typical of those of the present catalysts as described above. The tpr spectrum, Figure 12, indicates the formation of anionic vacancies on the CeO₂ surface by the reduction of surface anion of CeO₂ at very low temperatures. The activity of the catalyst measured rich of stoichiometric at lambda=0.98 in a simulated gas mixture indicates significant low temperature performance for CO, NO and alkene compared to that indicated by standard Pt-Rh/Al₂O₃-CeO₂ catalyst, Figures 13-15. A similar effect is observed when the catalysts are tested under perturbed condition whose details are shown in Table 6 below. The perturbed activity of the Pt-Pd-CeO₂ catalyst is significantly higher than the standard catalyst, especially at low temperature, Figures 16-18.

Table 6

5 **Frequency = 0.5Hz Amplitude +/- 1 A/F Average $\lambda = 1.01$**

	<u>Composition</u>	<u>Concentration / mol%</u>
10	CO	0.85
	CO ₂	15.0
15	NO	0.15
	H ₂	0.28

20 **Frequency = 0.5Hz Amplitude +/- 1 A/F Average $\lambda = 1.01$**

	<u>Composition</u>	<u>Concentration / mol%</u>
25	O ₂	0.92
	CH ₄	0.0446
30	C ₃ H ₈	0.015
	C ₃ H ₆	0.015
35	SO ₂	0.002
	H ₂ O	9.0

40 Alternate addition of CO and O₂ to the above gas mixture at a frequency of 0.5Hz.
Rich inject 3.11% CO to achieve CO = 3.96% ($\lambda = 0.94$).
Lean inject 1.41% O₂ to achieve O₂ = 2.33% ($\lambda = 1.08$).
When perturbing, CO stabilises at 2.33% and O₂ at 1.55% ($\lambda = 1.01$).

45 **EXAMPLE 6**

Pd-Pt-CeO₂-MO (MO=Al₂O₃) Catalyst made by co-precipitation using Ce³⁺ precursor

50 To increase the thermal stability of the co-precipitated catalyst, a second metal oxide was incorporated during the co-precipitation process. The role of the secondary metal oxide is to decrease the extent of CeO₂ sintering during high temperature exposure.

50g of a 4%Pd-0.5%Pt-10%Al₂O₃-CeO₂ catalyst were made by the co-precipitation technique described in Example 2, using Ce(NO₃)₃ (126g), Al(NO₃)₃.9H₂O (69g), Pd(NO₃)₂ (25g), H₂PtCl₆ (0.64g) and NaOH (62.56g). The metal salts were dissolved as a single solution and added dropwise to the boiling NaOH.

55 To illustrate the stabilisation effect of Al₂O₃, BET surface areas of the catalyst were measured after calcination in air at 900°C. The values are given in Table 7.

Table 7

Catalyst Calcined 900°C	BET Surface Area, m ² g ⁻¹
4%Pd-0.5%Pt-CeO ₂	12.5
4%Pd-0.5%Pt-10%Al-CeO ₂	64.0

The stabilising effect of alumina is also shown on the tpr profiles of the samples calcined at 900°C, Figures 19-20. The sample without Al₂O₃ has sintered significantly as shown by the increase in the bulk reduction peak (high temperature) relative to the surface reduction peak (low temperature). However, for the Al₂O₃ doped sample, significant surface reduction peak is maintained. Similarly the Al₂O₃ doped sample maintains significant low temperature activity even after calcination at 900°C, Figure 21.

EXAMPLE 7

Pt-MO (MO=CeO₂, SnO₂) Catalyst made by co-precipitating Pt colloid with Ce⁴⁺ or Sn⁴⁺ precursor

In this preparative route, the source of small metal particles is pre-formed metal colloids.

To make 50g of 0.9wt% Pt-CeO₂ catalyst, 166g of ceric ammonium nitrate (NH₄)₂Ce(NO₃)₆ was dissolved in 500cm³ of H₂O. A Pt sol was prepared to contain 2.1g Pt per litre, and 215cm³ of the sol was diluted to 500cm³ with distilled water. 73g of crystalline NaOH was dissolved in 6 litres of water and brought to the boil. The Pt sol and ceric solution were added separately at a constant flow rate to the NaOH solution. After complete addition, the precipitate was boiled for an hour prior to filtration, washing, drying and calcination in air at 500°C.

Similarly, to make 50g of 0.9wt% Pt-SnO₂ catalyst, 116.3g SnCl₄.5H₂O was dissolved in 500cm³ of H₂O. 215cm³ of a Pt sol of known concentration, 2.1g Pt per litre, was diluted to 500cm³ with de-ionised water. 54g of crystalline NaOH was dissolved in 6 litres of water and brought to the boil. The Pt sol and the Sn(IV) solution were added to the boiling NaOH separately, but simultaneously, and at a constant flow rate. The grey precipitate was boiled for an hour after complete addition of the precursor solutions. The precipitate was filtered hot, then washed, dried and calcined in air at 500°C.

The Pt-CeO₂ catalyst, made by this preparative route, has a reduction profile, Figure 22, indicative of the strong metal-metal oxide interaction identified by promotion of reduction of surface anion at low temperature, which indicates the formation of anionic vacancies on the CeO₂ surface. Similarly, the catalyst can promote CO, NO and alkene conversion at low temperature in a simulated exhaust condition rich of stoichiometric at lambda=0.98, Figure 23. The Pt-SnO₂ catalyst will promote low temperature conversion of CO and alkene when under lean of stoichiometric.

EXAMPLE 8

M-ZrO₂ (M=Au, Pt or Pd) Catalyst made by co-precipitation in the presence of a reducing agent

In this preparative route, the small particles of the metal are formed in situ, by the action of a reducing agent on hydrolysed salt of the metal.

50g of 4.0wt% Au-ZrO₂ catalyst was prepared using ZrOCl₂.8H₂O (130.71g), HAuCl₄ (4.059g - assay 49.27wt% Au), NaOH pellets (40.97g) and HCOONa (1.66g). The zirconyl chloride and auric acid were dissolved together in 500cm³ of water, whilst the sodium hydroxide and sodium formate were dissolved in a similar volume of water. These two solutions were added separately, but at the same rate and simultaneously, to 6 litres of boiling distilled water, whilst maintaining a constant pH of 7. After complete addition, the purple gelatinous precipitate was boiled for a further fifteen minutes, prior to filtration, washing, drying and calcining at 500°C.

The Au-ZrO₂ catalyst prepared by the above route is capable of converting CO and NO at low temperature in a simulated exhaust gas mixture, rich of stoichiometric at lambda=0.98, Figure 24. The strong Au-ZrO₂ interaction achieved through this preparative route is demonstrated by the presence of low temperature reduction peak in the tpr profile, which indicates the formation of anionic vacancies on the ZrO₂ surface; a corresponding catalyst made by impregnation consumes H₂ at higher temperature - Figure 25 (NB, a Au-Al₂O₃ catalyst made by impregnation, after calcination at 500°C, does not show any H₂ consumption during tpr, indicating that the reduction peak of the Au-ZrO₂ system is not due to reducibility of the Au species, which should be present in a metallic state).

COMPARATIVE EXAMPLE

5 A catalyst containing 0.9% Pt and 20% CeO₂ was prepared by conventional impregnation of conventional Al₂O₃-CeO₂ with a Pt precursor and then calcination at 500°C. The catalyst was tested for its ability to convert CO, NO and alkene in the same way as were the catalysts described in Example 2. The results for this comparative are shown in Figure 26. Comparison with Figures 5-7 shows the greater low temperature activity of the catalyst of the invention.

10 Claims

1. A method of conducting a chemical reaction comprising the oxidation of carbon monoxide to carbon dioxide employing a catalyst composed of metal oxide particles among which are uniformly incorporated noble metal particles, the catalyst having such a high interaction between the noble metal particles and the metal oxide particles that, without hydrogen reduction pre-treatment, it exhibits the formation of anionic vacancies on the metal oxide surface at a temperature lower than does the corresponding catalyst, without hydrogen reduction pre-treatment, containing the same amount of the metal oxide particles and noble metal particles and prepared by impregnating the metal oxide particles with noble metal precursor and calcining to convert the precursor to the noble metal particles.
2. A method according to claim 1 wherein the catalyst is employed without hydrogen reduction pre-treatment.
3. A method according to claim 1 or 2 wherein the catalyst is employed after a calcination pre-treatment in air at between 500 and 900°C.
4. A method according to any one of the preceding claims wherein the reaction is the oxidation of carbon monoxide and hydrocarbon to carbon dioxide and water and the reduction of nitrogen oxides to nitrogen.
5. A method according to claim 4 which occurs in the exhaust apparatus of an engine, in order to combat air pollution.
6. A method according to claim 5 wherein the engine is an internal combustion engine in a vehicle.
7. A method according to any one of the preceding claims wherein the catalyst contains 0.1 to 30% by weight of the noble metal particles based on the total weight of the noble metal particles and the metal oxide particles.
8. A method according to any one of the preceding claims wherein the noble metal particle diameter is less than 10Å.
9. A method according to any one of the preceding claims wherein the metal oxide particle diameter is up to 250Å.
10. A method according to any one of the preceding claims wherein the noble metal is one or more of Pt, Pd and Rh.
11. A method according to any one of the preceding claims wherein the metal oxide comprises one or more of CeO₂, ZrO₂, TiO₂ and SnO₂.
12. A method according to any one of the preceding claims wherein the catalyst is preparable by co-precipitation of the noble metal particles and the metal oxide particles.
13. A method according to any one of the preceding claims wherein the metal oxide comprises CeO₂.
14. An engine whose exhaust apparatus contains the catalyst defined in any one of the preceding claims in order to combat air pollution.
15. An engine according to claim 14 which is an internal combustion engine in a vehicle.
16. A catalyst defined in claim 13 wherein the noble metal is one or more of Pt, Pd, Rh and Au.
17. A process for preparing a catalyst composed of metal oxide particles comprising CeO₂ among which are uniformly incorporated noble metal particles, the noble metal being one or more of Pt, Pd, Rh and Au, which process comprises co-precipitating the noble metal particles and the metal oxide particles comprising CeO₂.
18. A process according to claim 17 wherein in the co-precipitation the noble metal particles are co-precipitated from colloid of the metal.
19. A process according to claim 18 wherein the co-precipitation is effected by admixing the noble metal colloid, a solution of metal oxide precursor, and a base.
20. A process according to claim 19 wherein the noble metal colloid is formed in situ by a reducing agent.
21. A process according to claim 17 wherein in the co-precipitation the noble metal particles are co-precipitated by reduction of hydrolysed noble metal salt.
22. A process according to claim 21 wherein the reduction is brought about by Ce³⁺ salt in solution.
23. A process according to claim 22 wherein the noble metal is one or more of Pt, Pd and Au.

24. A process according to any one of claims 17-23 wherein the co-precipitation is brought about by reaction of a solution of a base and a solution of metal oxide precursor.

25. A process according to claim 24 wherein the solution of metal oxide precursor is added to the solution of the base.

5 26. A process for preparing ceria, which process comprises adding a solution of ceria precursor to a solution of a base to precipitate cerium hydroxide and heating the cerium hydroxide to convert it to ceria.

27. A method of conducting a chemical reaction employing a catalyst claimed in claim 16.

28. A method according to claim 27 wherein the catalyst is employed without hydrogen reduction pre-treatment.

10 29. A method according to claim 27 or 28 wherein the catalyst is employed after a calcination pre-treatment in air at between 500 and 900°C.

30. A method according to any one of claims 27-29 wherein the reaction is a redox reaction.

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Fig 1a.

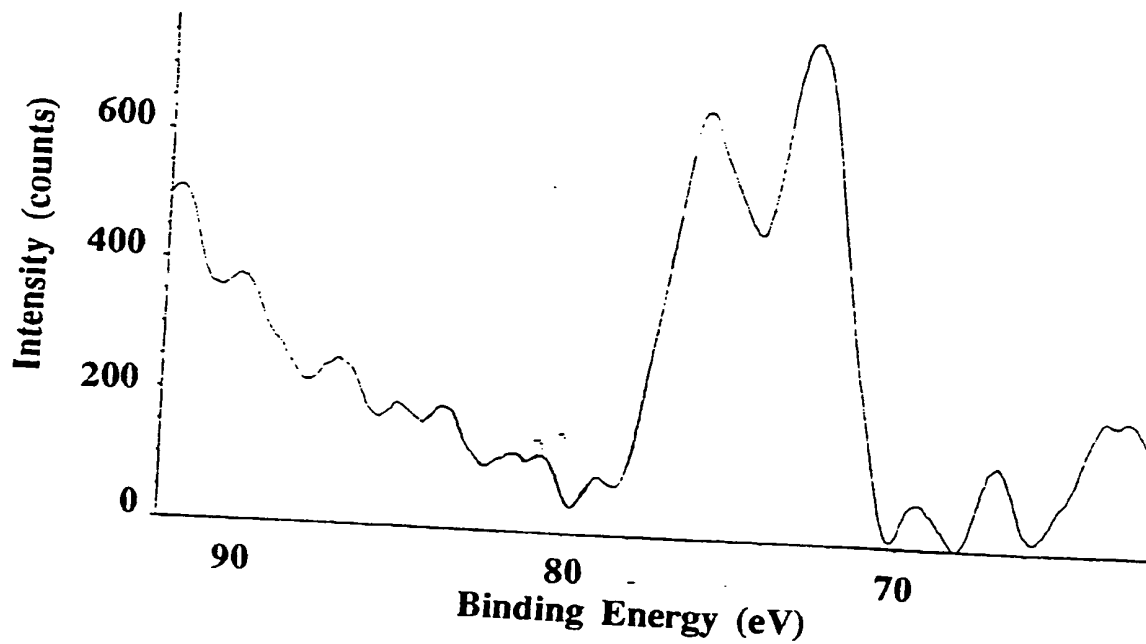
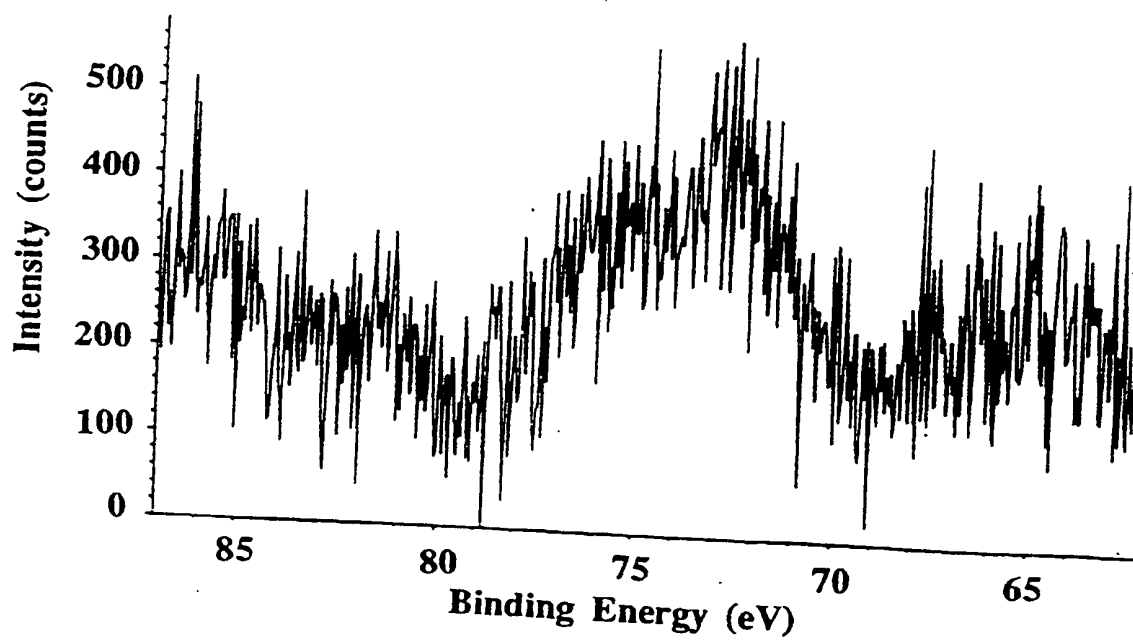


Fig 1b.



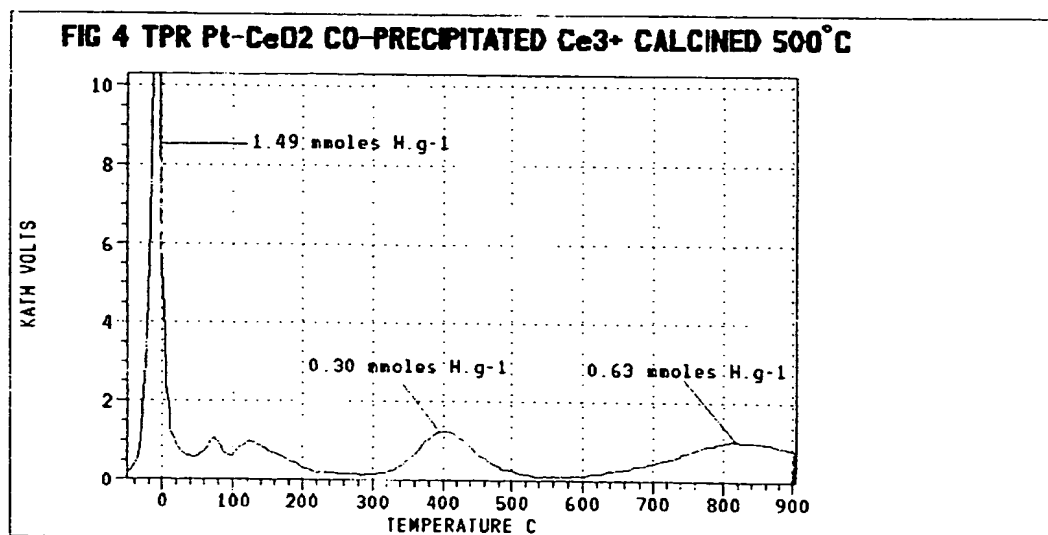
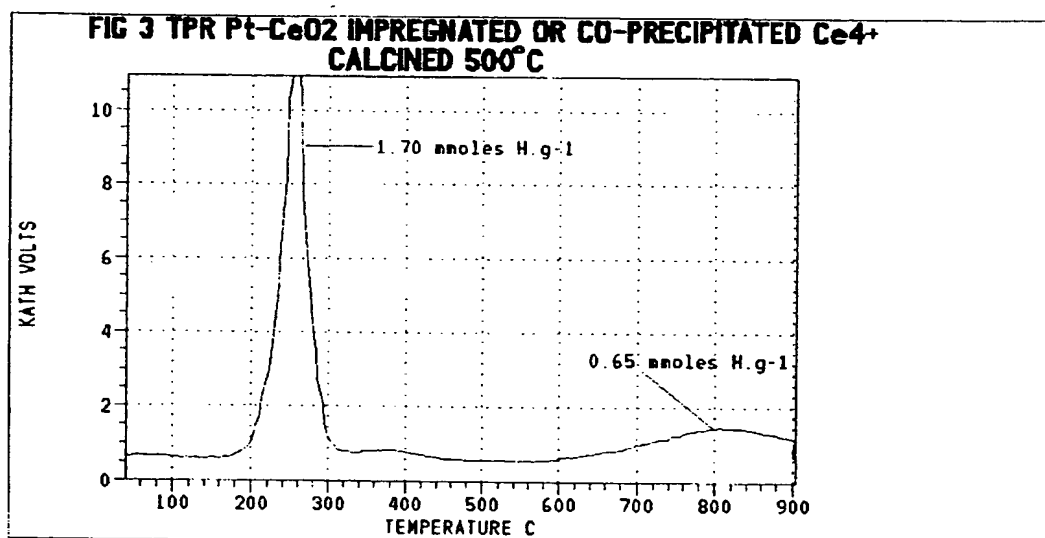
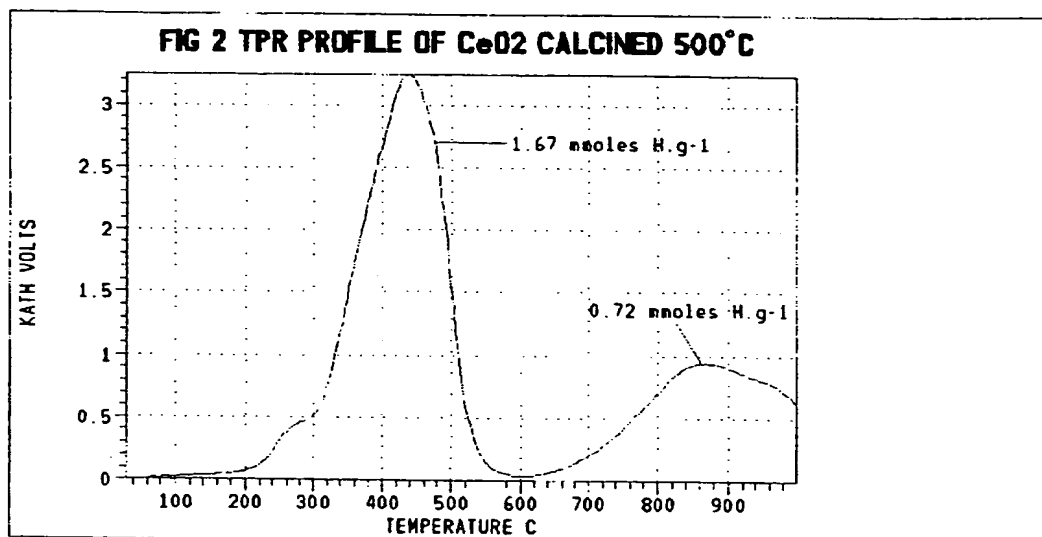


Fig 5 Rich CO Activity of 0.9%Pt-CeO₂ Calcined at 500°C
Lambda = 0.98

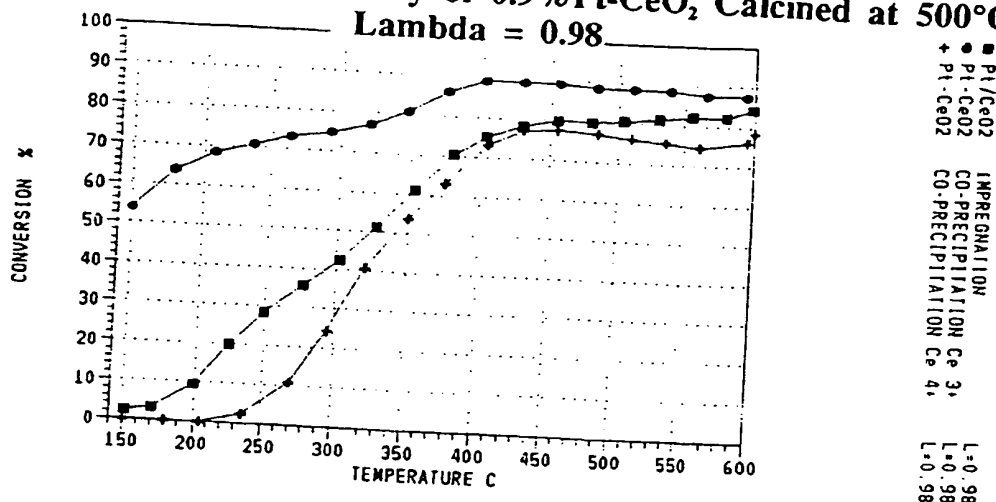


Fig 6 Rich NO_x Activity of 0.9%Pt-CeO₂ Calcined at 500°C
Lambda = 0.98

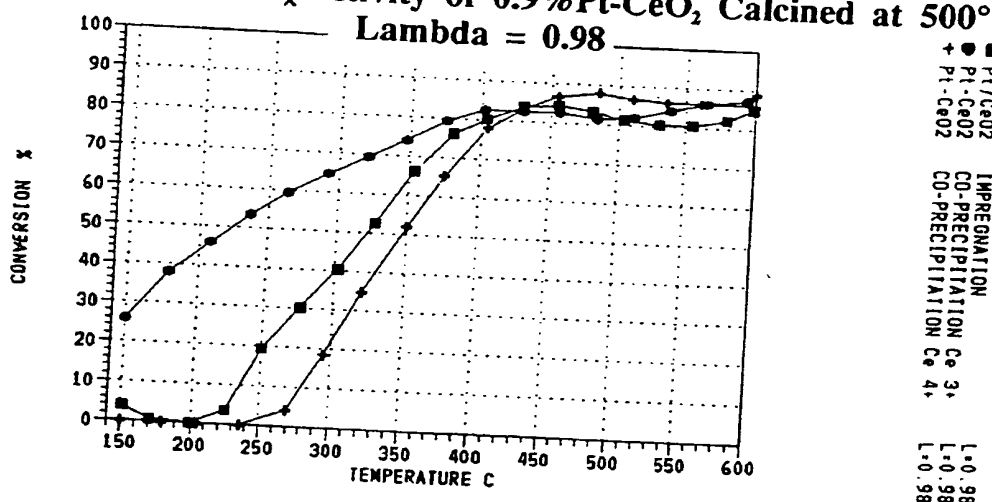
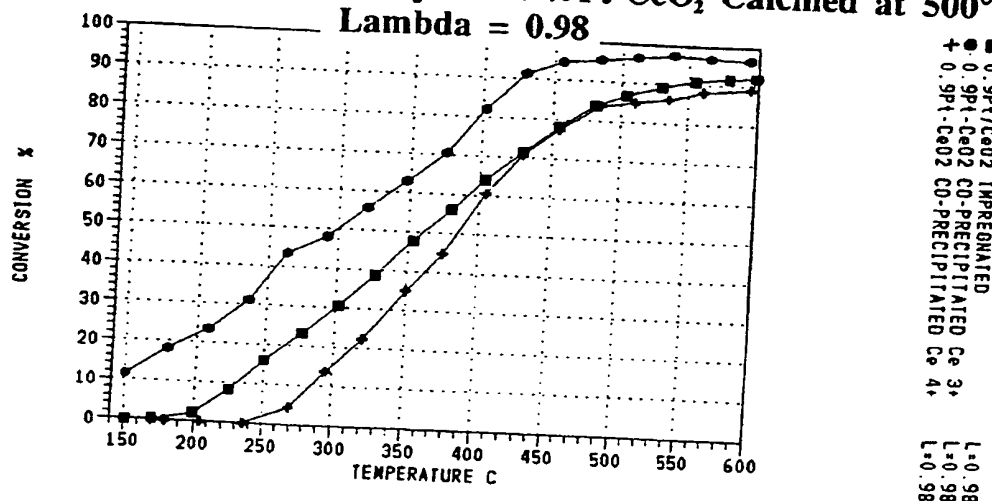
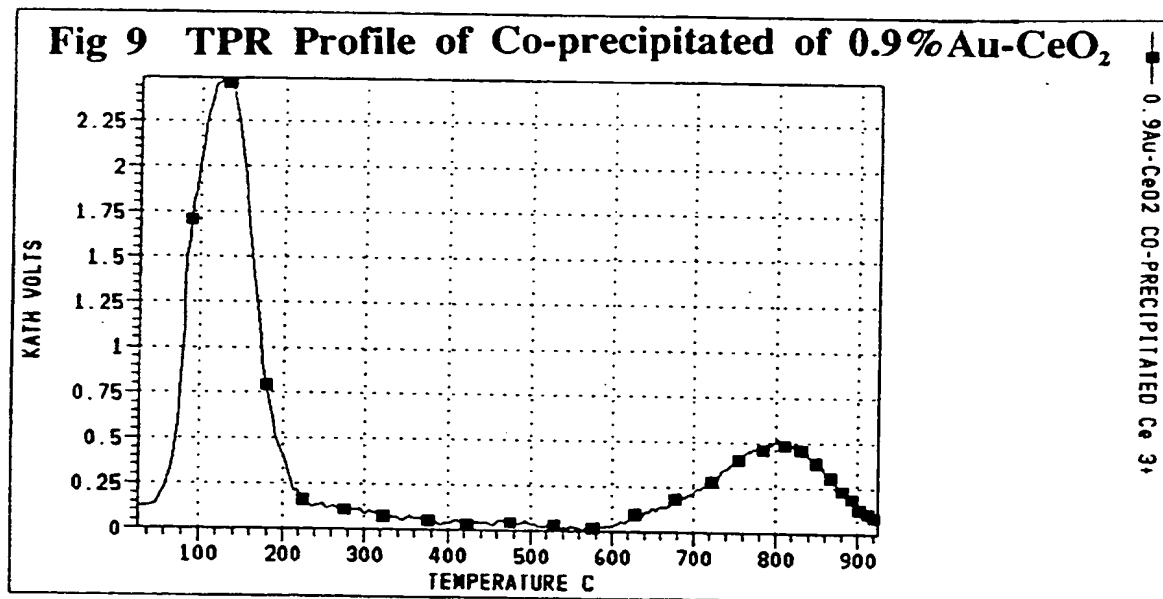
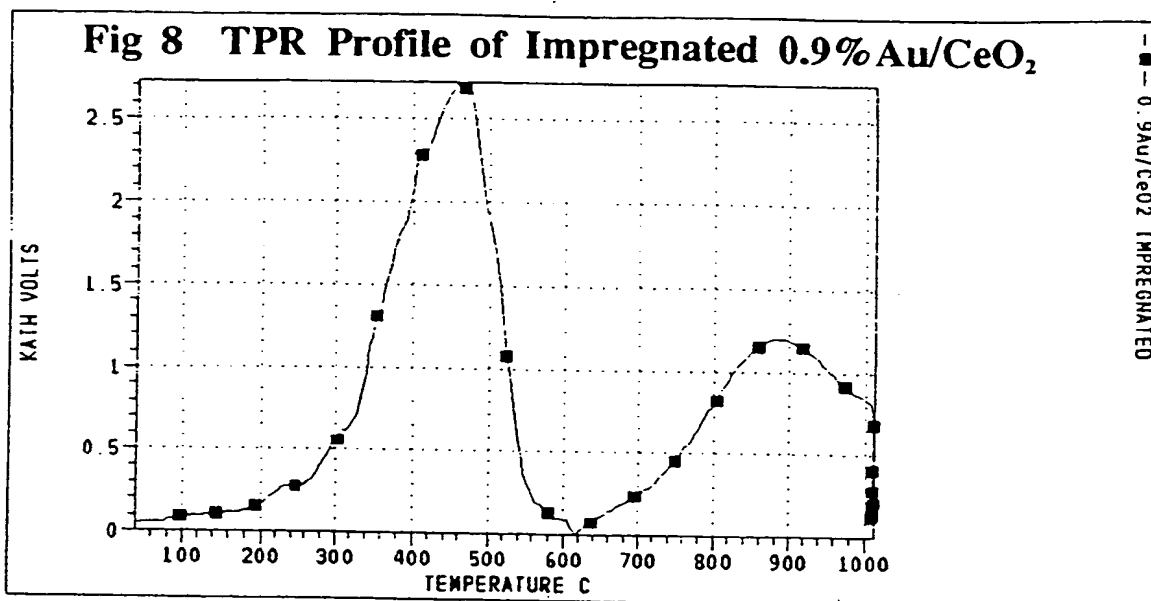
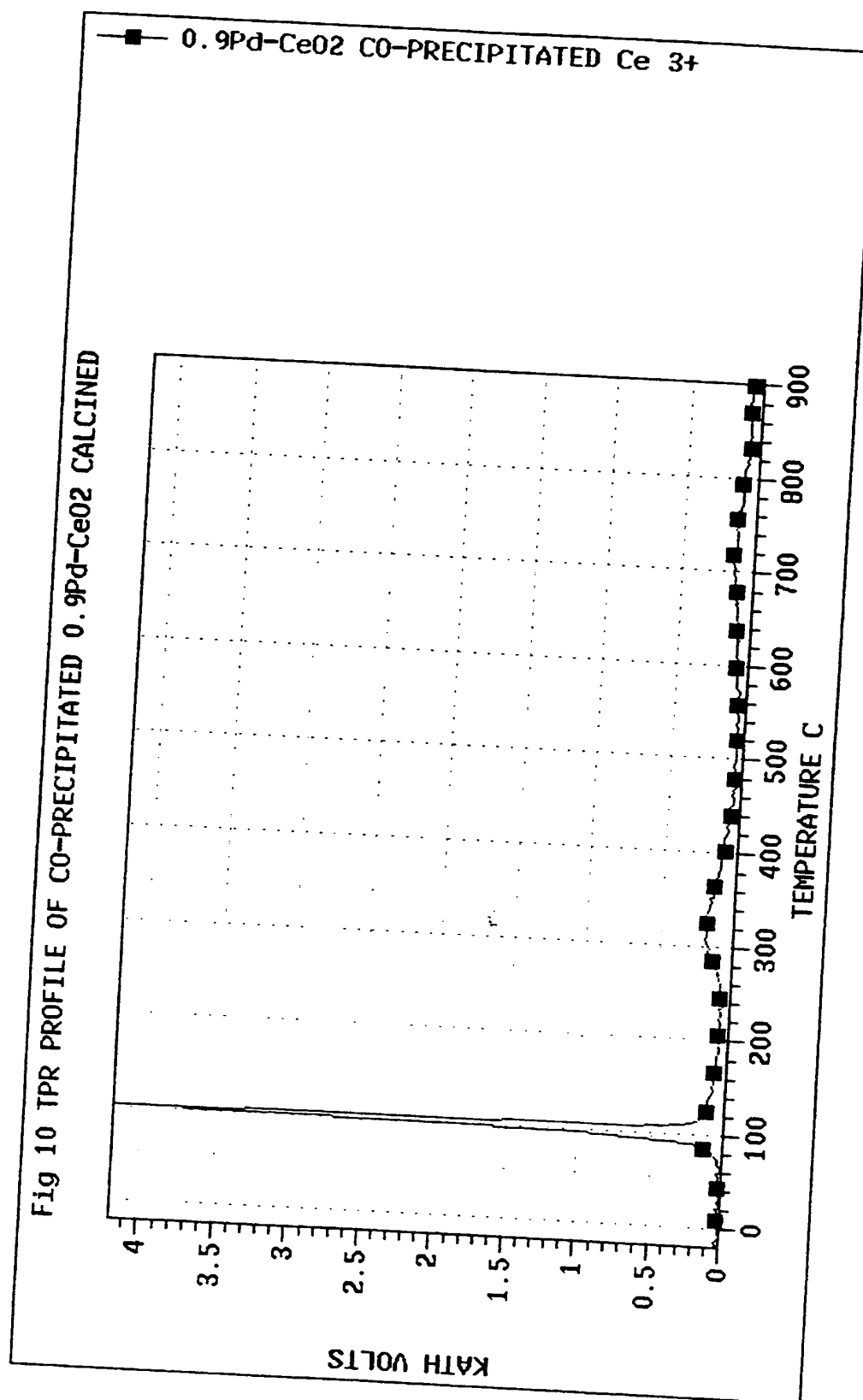
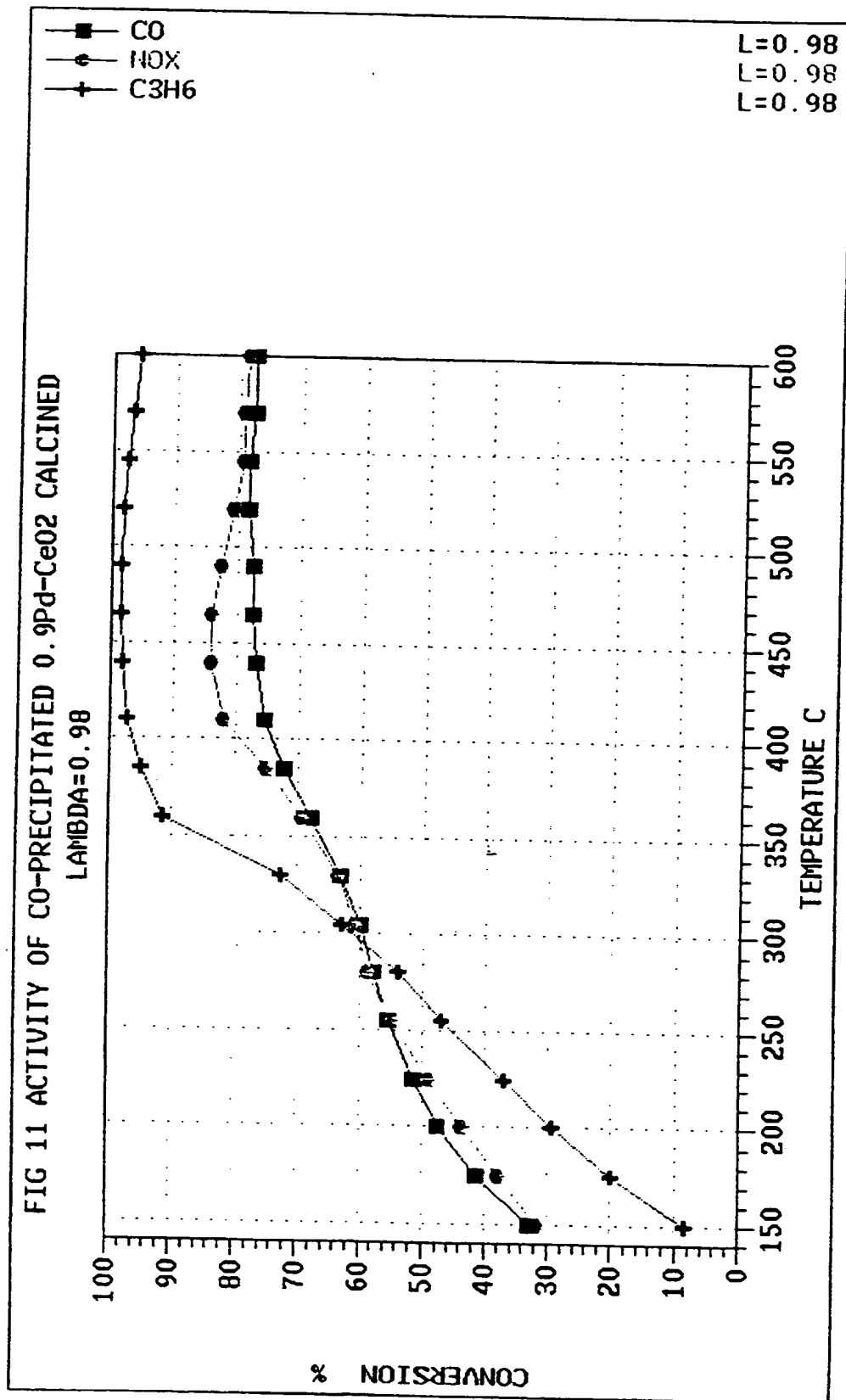


Fig 7 Rich C₃H₆ Activity of 0.9%Pt-CeO₂ Calcined at 500°C
Lambda = 0.98









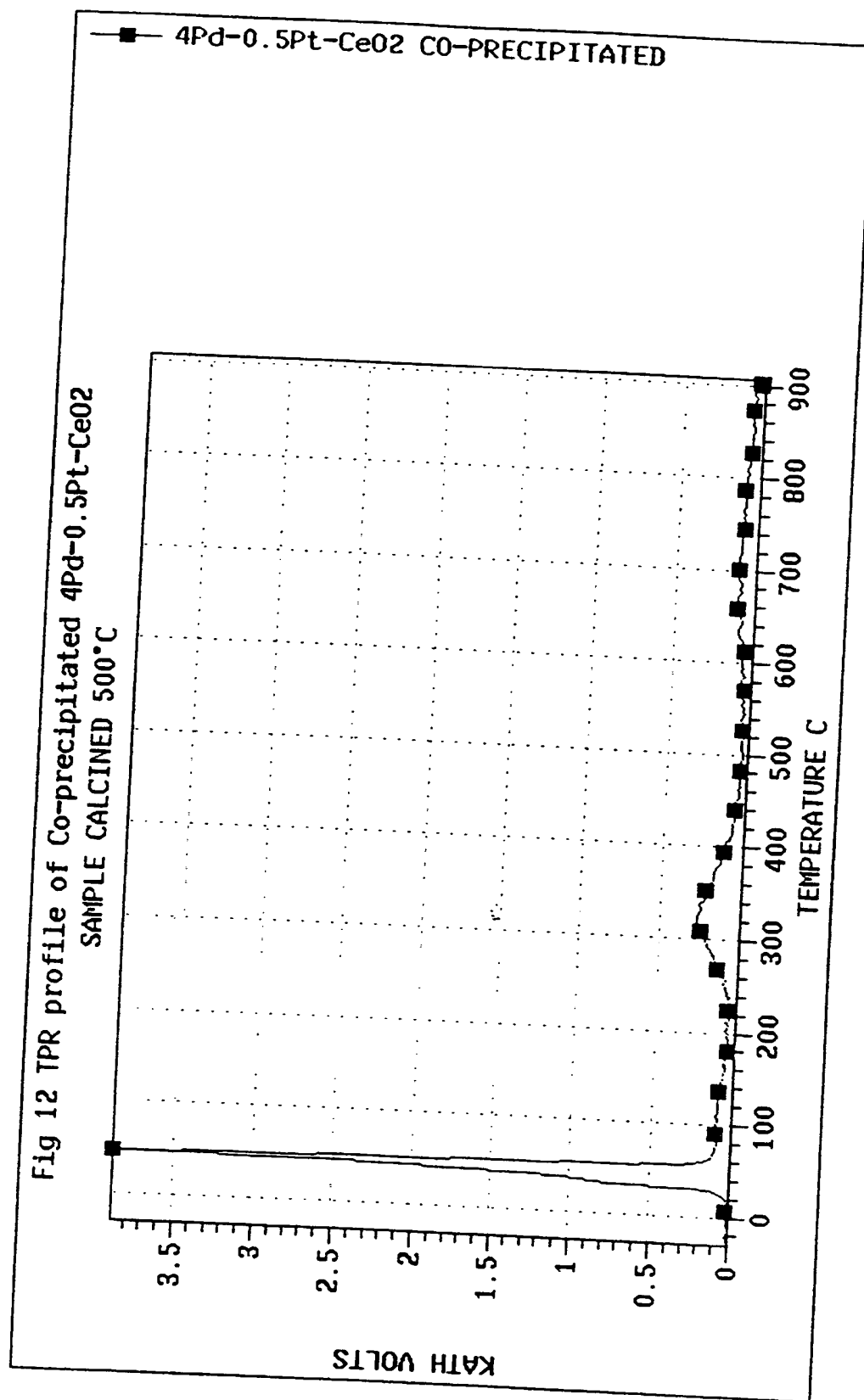
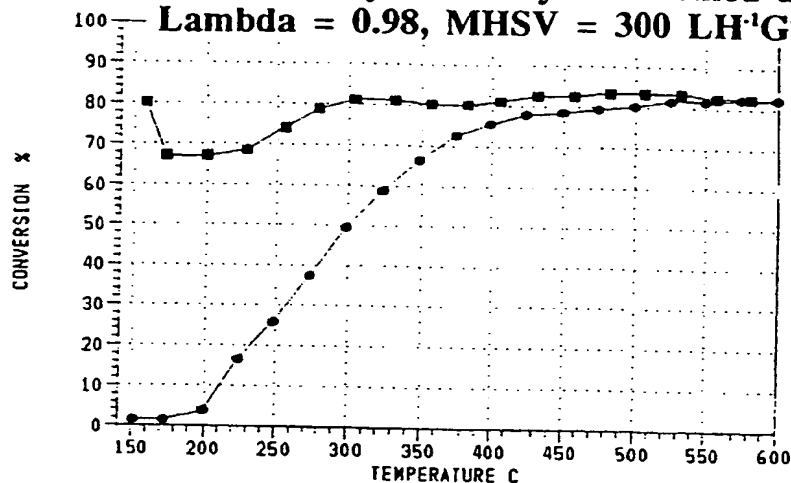
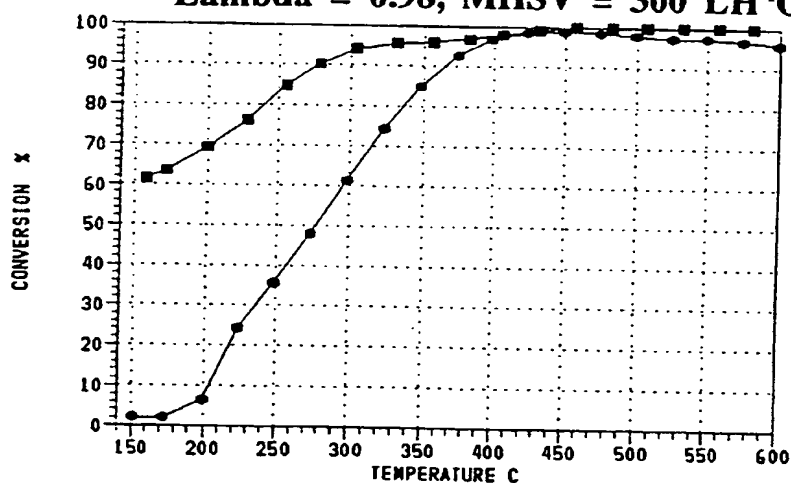


Fig 13 CO Activity of Catalysts Calcined at 500°C
Lambda = 0.98, MHSV = 300 LH⁻¹G⁻¹



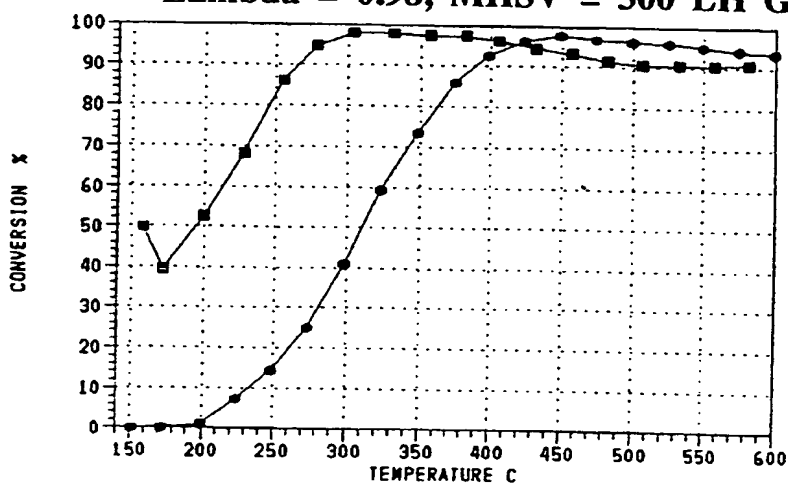
—■— 4Pd-0.5Pt-CeO₂ CO-PRECIPIATION Ce 3+
 —●— 0.18Rh-0.9Pt/Al₂O₃-CeO₂ L=0.98

Fig 14 NO_x Activity of Catalysts Calcined at 500°C
Lambda = 0.98, MHSV = 300 LH⁻¹G⁻¹



—■— 4Pd-0.5Pt-CeO₂ CO-PRECIPIATION Ce 3+
 —●— 0.18Rh-0.9Pt/Al₂O₃-CeO₂

Fig 15 C₃H₆ Activity of Catalysts Calcined at 500°C
Lambda = 0.98, MHSV = 300 LH⁻¹G⁻¹



—■— 4Pd-0.5Pt-CeO₂ CO-PRECIPIATION Ce 3+
 —●— 0.18Rh-0.9Pt/Al₂O₃-CeO₂ IMPREGNATION

Fig 16 Perturbed CO Activity of Catalysts Calcined at 500°C
Perturbation Frequency 0.5Hz, Amplitude 1A/F

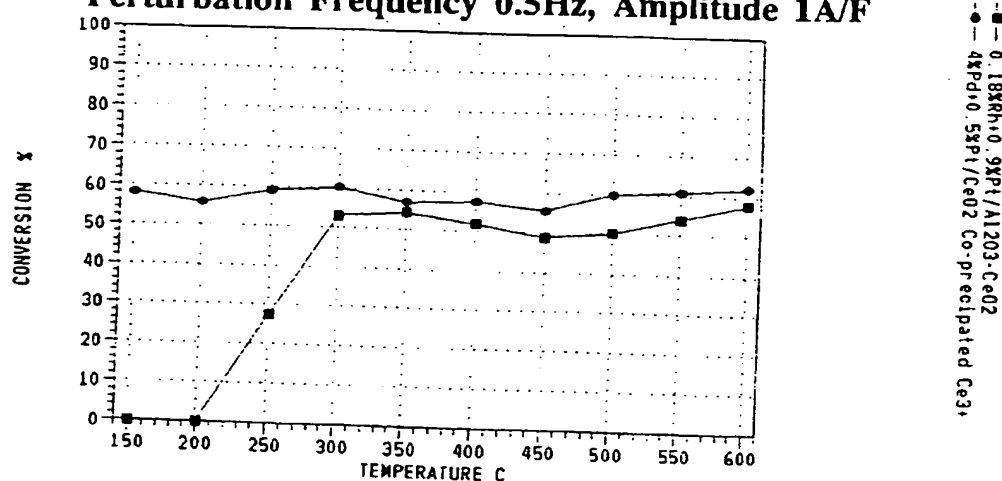


Fig 17 Perturbed NO_x Activity of Catalysts Calcined at 500°C
Perturbation Frequency 0.5Hz, Amplitude 1A/F

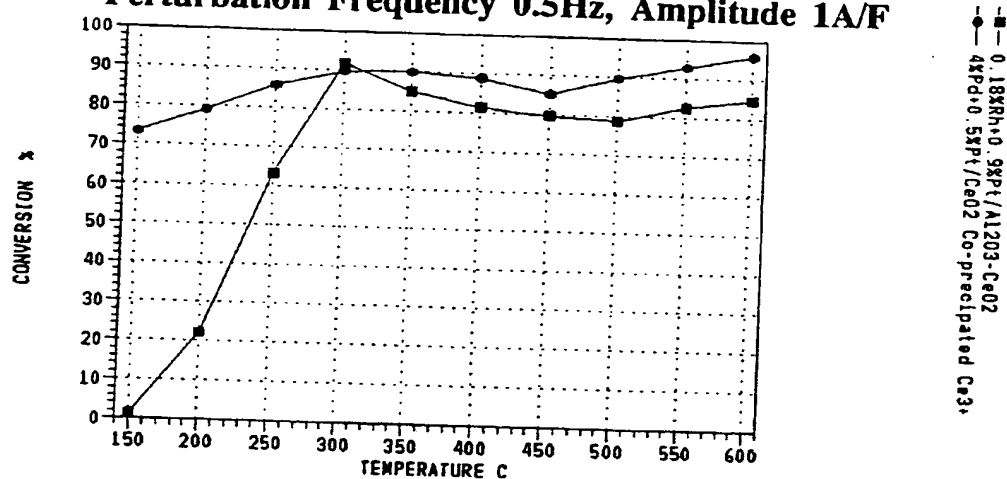


Fig 18 Perturbed C₃H₆ Activity of Catalysts Calcined at 500°C
Perturbation Frequency 0.5Hz, Amplitude 1A/F

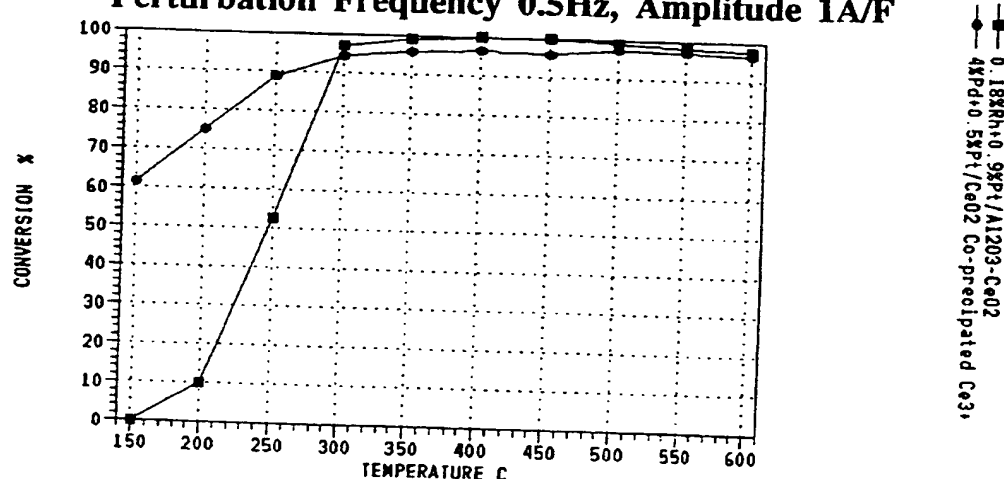
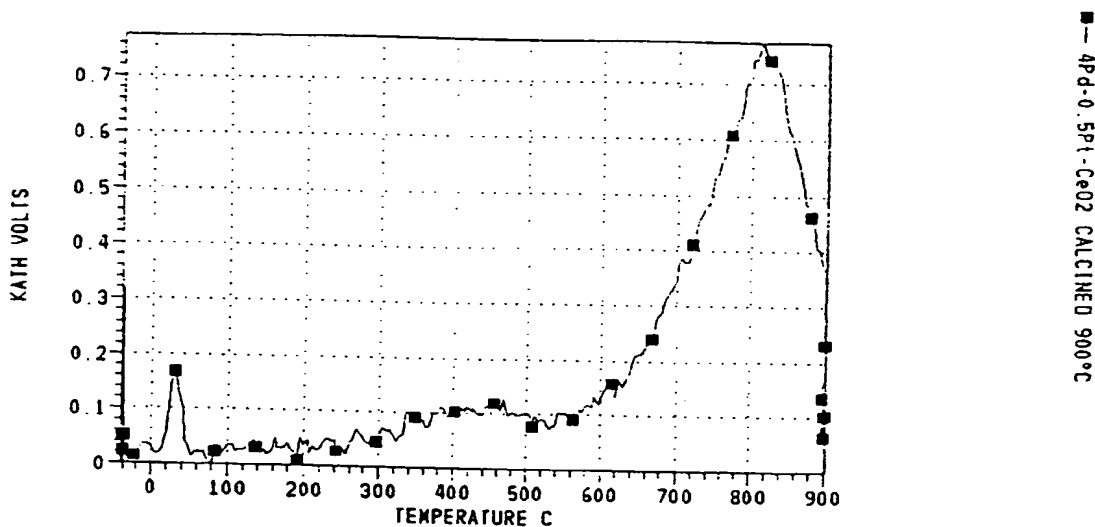
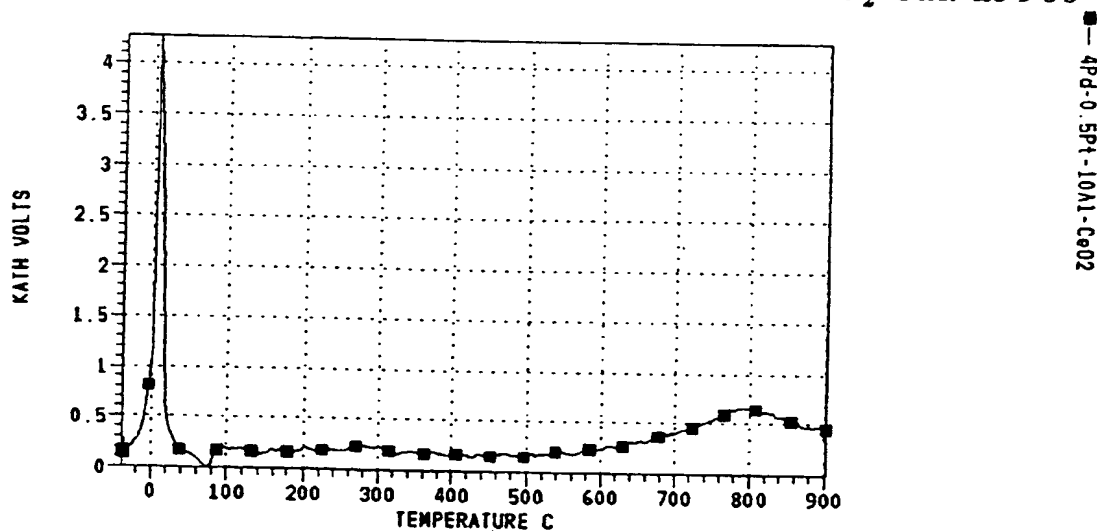
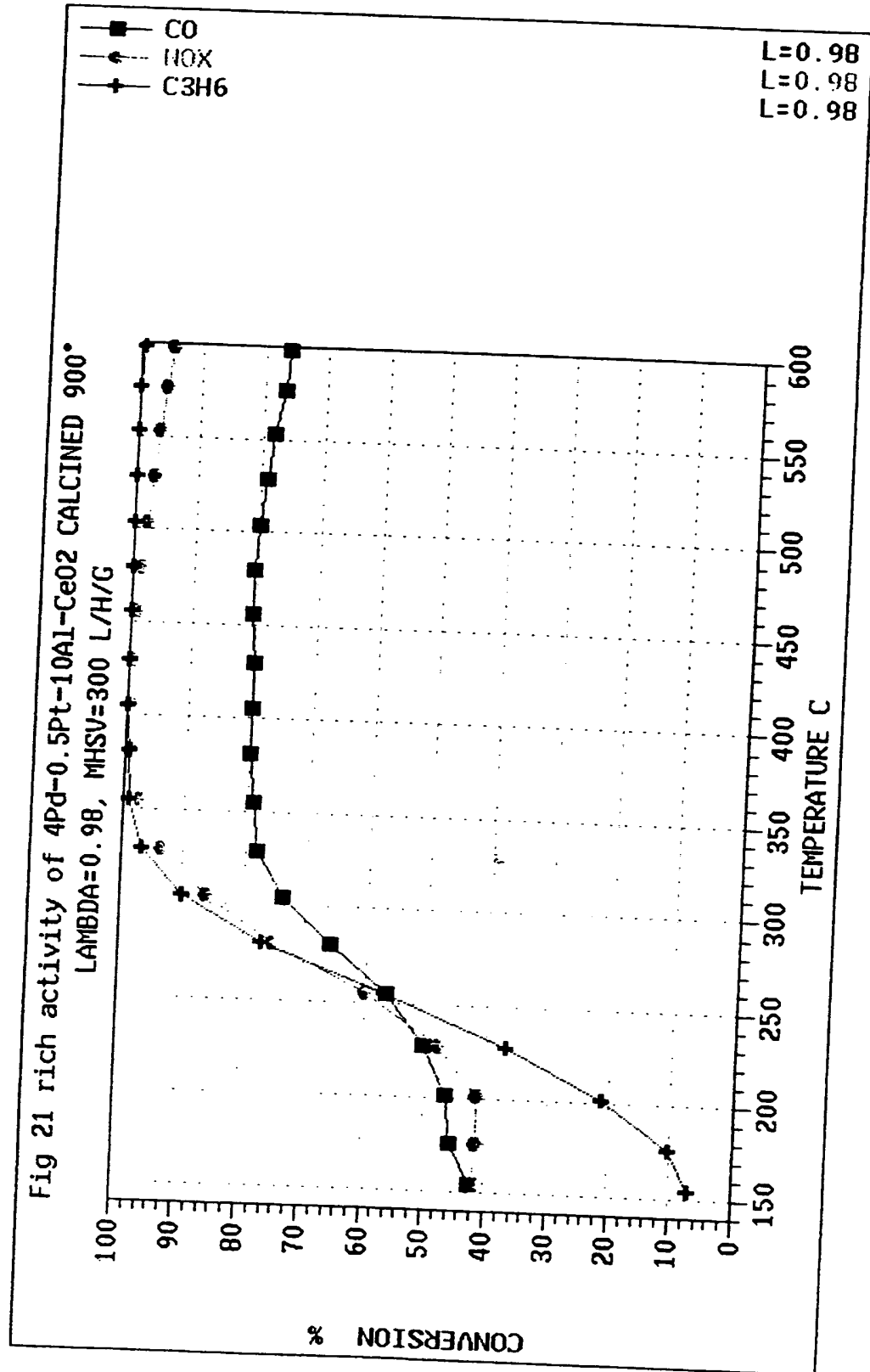
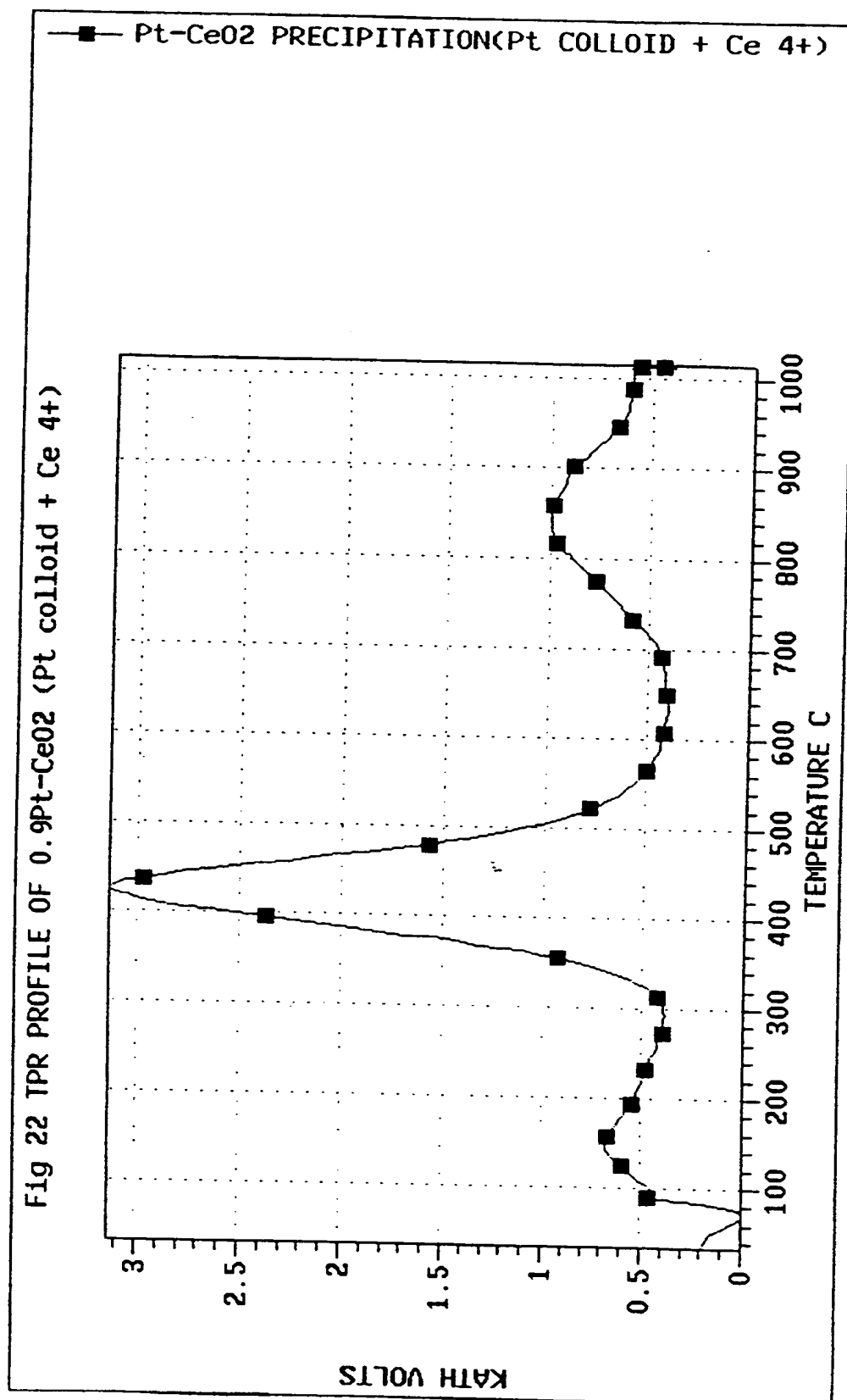
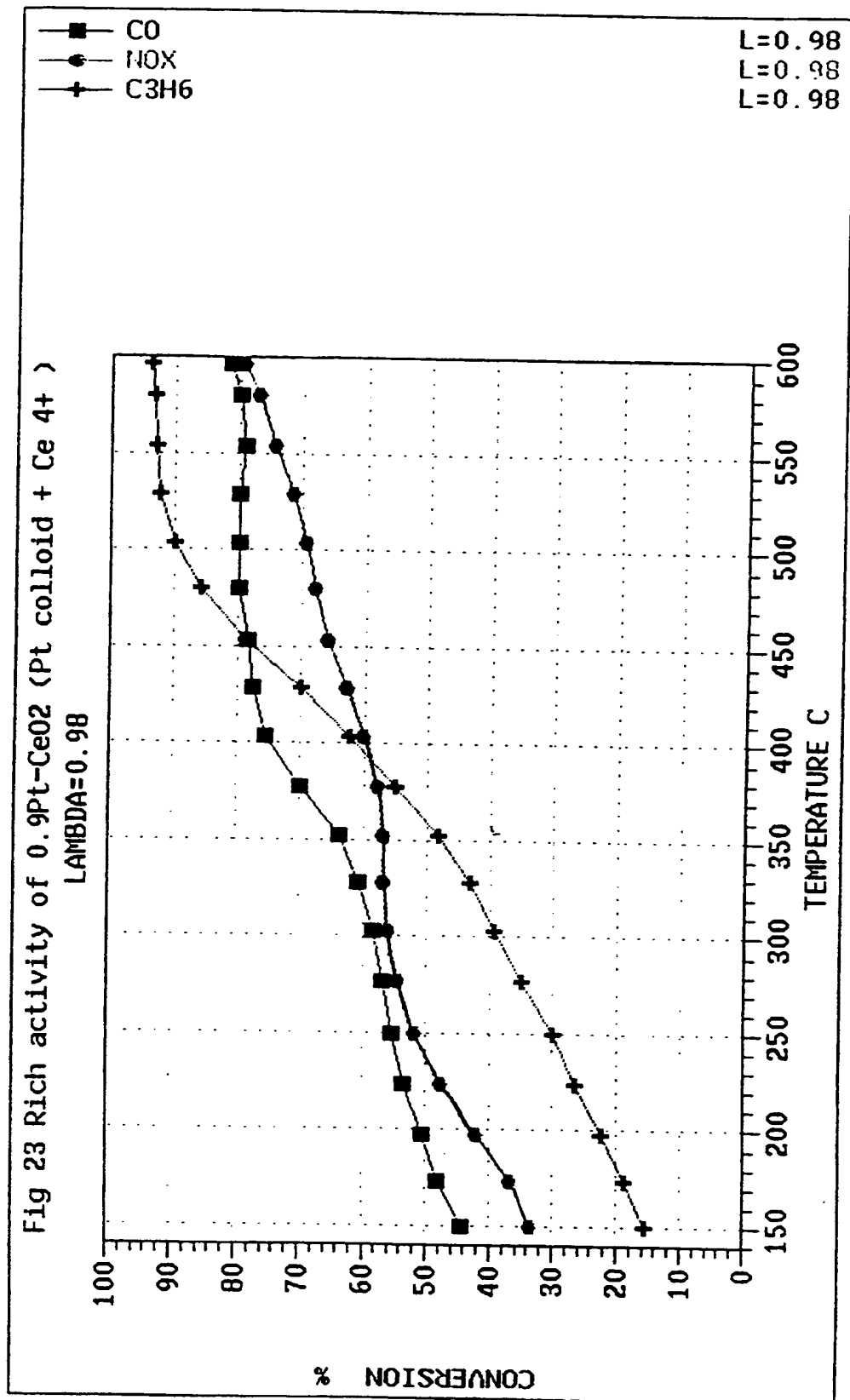
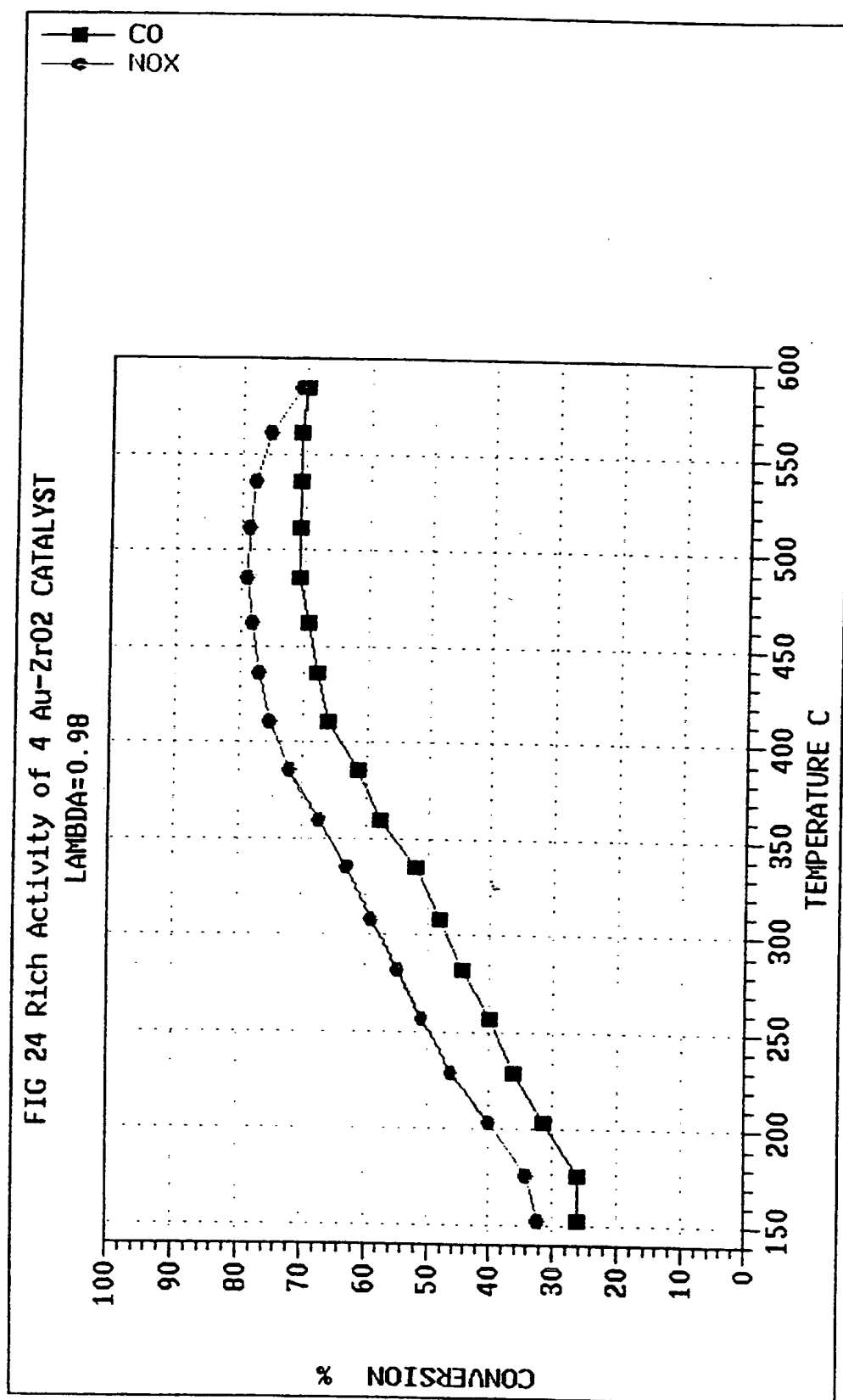


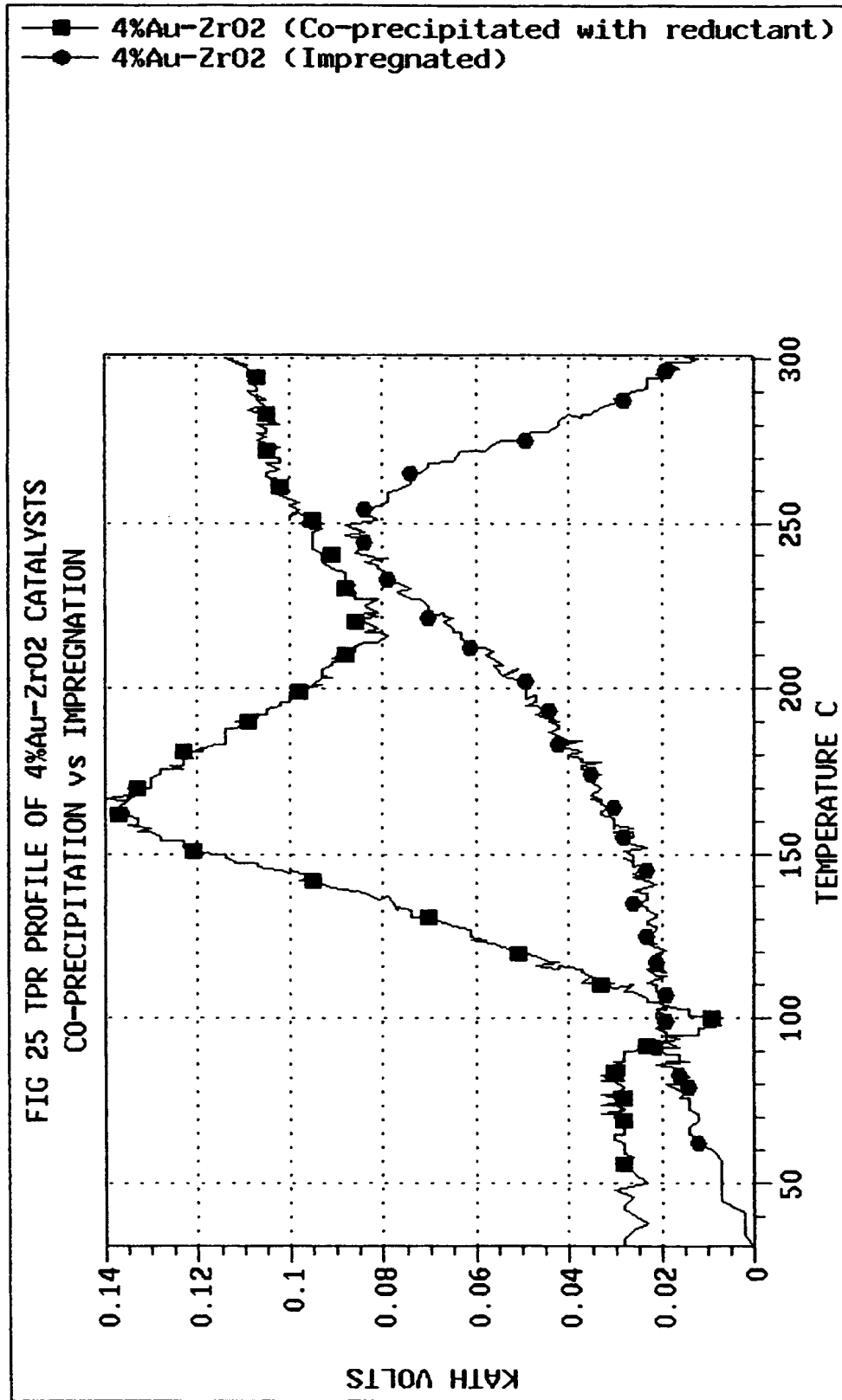
Fig 19 TPR Profile of 4%Pd-0.5%Pt-CeO₂ Calcined at 900°C**Fig 20 TPR Profile of 4%Pd-0.5%Pt-10%Al-CeO₂ Cal. at 900°C**

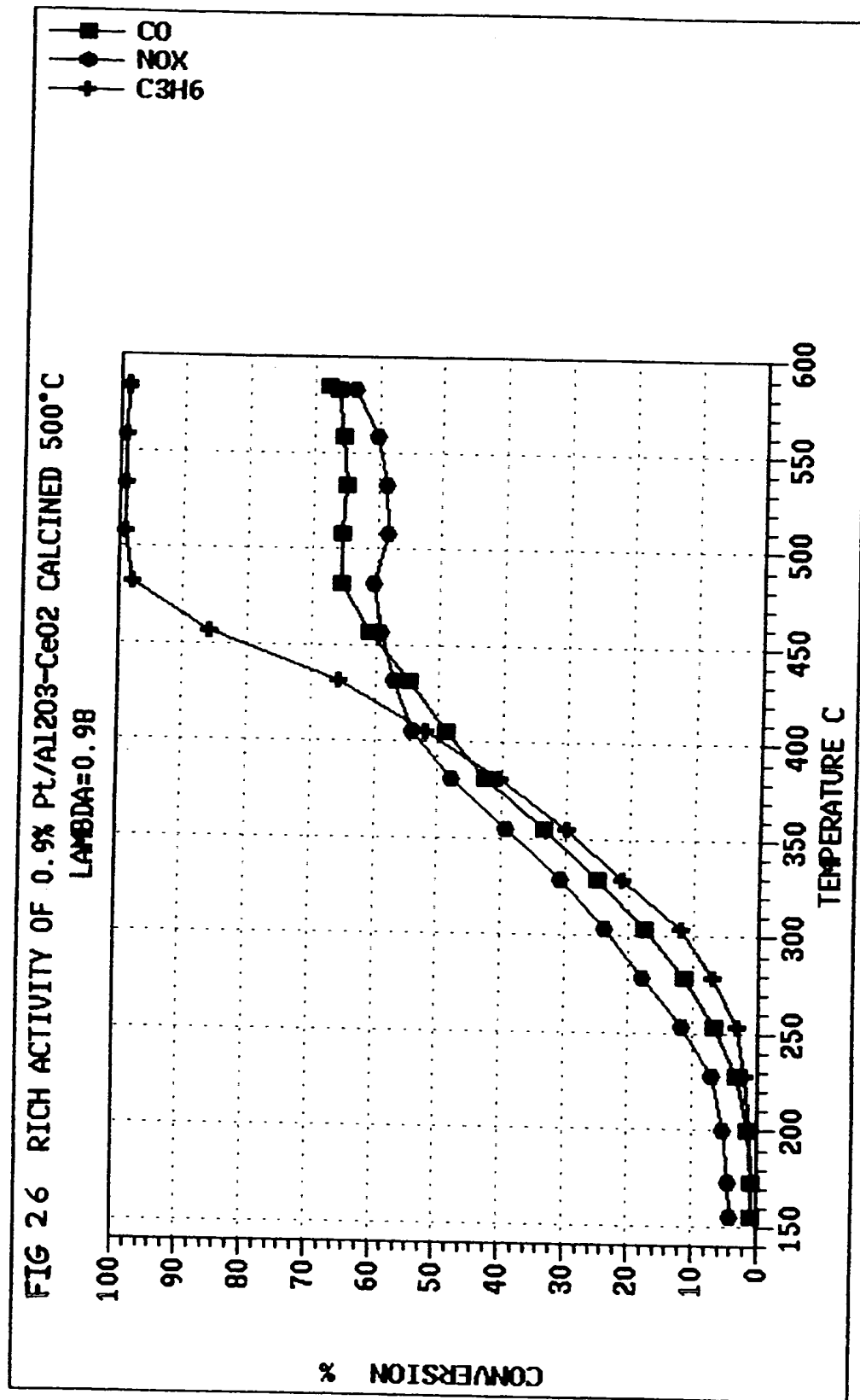














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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 9782

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	EP-A-0 499 402 (PHILIP MORRIS PRODUCTS INC.) * page 3, line 42 - page 5, line 33; claims 1-26 *	1-7, 10-12, 14,15	B01D53/36 B01J23/56 B01J37/03
Y	----	17-25	
X	EP-A-0 461 950 (RHONE-POULENC CHIMIE) * page 2, line 44 - line 53; claims 1-36 *	26-29	
Y	----	17-25	
X	GB-A-2 122 912 (JOHNSON MATTHEY PLC) * claims 1-10; example 1 *	1,2,4-7, 10-17	
A	DE-A-38 32 268 (AGENCY OF INDUSTRIAL SCIENCE & TECHNOLOGY) * column 6, line 55 - column 15, line 31; claims 1-33; examples 1-19 *	1-25	
A	EP-A-0 428 753 (N.E. CHEMCAT CORP.) * page 2, line 34 - page 5, line 6; claims 1-16 *	1-28	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 March 1994	Examiner Eijkenboom, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

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